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STA_____ E ORGANICS IN ENVIRONMENTAL WATER SAMPLES: STORAGE AND PRESERVATION

Final Report

August 1989

M. P. Maskarinec
C. K. Bayne
L. H. Johnson
S. K. Holladay
R. A. Jenkins

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STABILITY OF VOLATILE ORGANICS IN ENVIRONMENTAL WATER SAMPLES: STORAGE AND PRESERVATION

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EXECUTIVE SUMMARY

This report focuses on data generated for the purpose of establishing the stability of volatile organic compounds in environmental water samples. The study was carried out over a one year time frame and took into account as many variables as possible within the constraints of budget and time. The objectives of the study were: 1) to provide a data base which could be used to provide guidance on pre-analytical holding times for regulatory purposes; 2) to make an attempt to develop storage and preservation techniques which would maximize the allowable holding times, in order to facilitate laboratory analytical efficiency; 3) to provide a basis for the evaluation of data which is generated outside of the currently allowable holding times; and 4) to develop techniques for the production of stable, long-term reference materials for quality assurance purposes.

The experimental design consisted of three water samples: distilled-in-glass water, a groundwater, and a surface water. The analytes consisted of most of the commonly encountered volatile organic compounds. All analyses were carried out using methods similar to those in the USEPA Contract Laboratory Program. GC/MS was used for all determinations. All determinations were carried out in quadruplicate along with a storage blank. Two concentration levels were studied: nominally 50 μg/L and 500 μg/L. Samples were stored at two conditions, room temperature and under refrigeration (4°C). Samples were analyzed at intervals of 0, 3, 7, 14, 28, 56, 112, and 365 days. The MHT's were estimated by two statistical definitions.

A method for the preparation of large volumes of fortified water samples was developed which consisted of filling a Tedlar gas sampling bag with the sample, addition of the analytes in methanolic solution, and dispensing of aliquots into 40 mL VOA vials without introduction of headspace and with minimal mixing. This method is shown to produce individual aliquots with precision better than 5%, well within accepted bounds for the analytical method. This method is shown to have applicability in the preparation of performance evaluation samples for interlaboratory comparisons and method validation studies.

The data from this study indicates that most volatile organic compounds are stable in water for longer than 365 days. Exceptions to this statement include compounds prone to dehydrohalogenation (e.g., 1,1,2,2-tetrachloroethane) and compounds prone to biological degradation, particularly the volatile aromatics. The stability of the compounds was matrix dependent and storage condition dependent. The matrix dependency was primarily related to the preserved biological activity of the matrix. The samples showed greater stability at refrigerated temperature than at room temperature. Within the limits of this study, the minimum holding time for an environmental water sample prior to analysis for volatile organic compounds is about ten days, although for most of the compounds stability is not a problem up to 365 days.

Because of the fact that the degradation observed in this study could apparently be controlled by preservation with acid, a second study was conducted comparing three acids

for preservation of the samples. The same three water matrices were studied. Samples were preserved with hydrochloric acid (HCl), sodium bisulfate, and ascorbic acid. For the most part, all three acids effectively reduced the degradation and preserved the samples. However, based on this work, sodium bisulfate is recommended for the preservation of volatile organic compounds in environmental water samples for the following reasons: 1) this acid is readily available, inexpensive, and free from interferences; 2) it is non-corrosive and can be added to sampling vials prior their to transport to the field; 3) the pK is 1.91, ensuring that the pH of the sample will be reduced to just slightly less than 2 regardless of the amount added; 4) sodium bisulfate is readily soluble in the aqueous matrix; and 5) the additional ionic strength resulting from the addition of sodium bisulfate can actually improve the reliability of the analytical method by increasing purge efficiency. While both the HCl and ascorbic acid affected preservation of the samples, neither combines all of these advantages.

Several approaches were taken to estimate the maximum holding time (MHT) for each analyte because a standard definition for MHT has not been adopted by the Environmental Protection Agency (EPA). First, the windows specified in the analytical method for acceptable matrix spike recovery were used as a means of identifying the period of time during which a sample could be stored without producing data which would be outside of "control" limits. Second, a procedure recommended by the American Society for Testing and Materials (ASTM) was modified and applied to the data base. Third, a procedure developed by Environmental Science and Engineering (ESE) for the analysis of a similar data base was applied. Each of these approaches resulted in different estimates of the MHT due to the application of different statistical procedures for the three definitions. Therefore, decisions concerning stability depend on the objective of the individual evaluating the environmental data.

This report is intended to summarize the findings of the study in such a way as to allow individual decisions to be made regarding the quality of environmental data. The use of the data base may well be different for analyses conducted under RCRA, for example, than for those conducted under NPDES permit requirements. For this reason, the summary statistics for each replicate anaysis is presented in the appendices of this report.

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INTRODUCTION

During the past two decades, there has been a dramatic expansion of environmental legislation, including the Comprehensive Environmental Response, Compensation, and Liability Act; the Resource Conservation and Recovery Act; the Toxic Substances Control Act; the Clean Water Act; the Safe Drinking Water Act; the Marine Act; and, most recently, the Superfund Amendment and Reauthorization Act. One result of these regulatory measures has been a tremendous increase in the number of samples collected and distributed for analysis. One estimate is that federal, state, and local governments combined with private industry accounted for 500,000-700,000 samples in 1986. Furthermore, this number is growing at a rate of 25-40% per year (1). Obviously, this has put tremendous strain on the capacity of analytical laboratories. In many cases, samples are collected at a particular site, shipped to a central distribution point, and assigned to individual laboratories on the basis of capacity. All of this is done with relatively little knowledge of the stability of the samples, and maximum pre-analytical holding times have been established based on the best available information, much of which has been pieced together in a somewhat arbitrary fashion.

In order to provide consistent results from analytical laboratories nationwide, the United States Environmental Protection Agency (USEPA) has issued various analytical methods in the Federal Register to standardize analyses. Among the quality assurance needs in these methods is the requirement for reference samples to enable interlaboratory comparisons to be made. This work focuses on the development of a data base which allows documentation of the stability of volatile organics in water, for purposes of increasing the pre-analytical holding times and therefore reducing the cost associated with the analysis. Such a database can only be generated if methods are available for the preparation of multiple sample aliquots. Thus, a major aspect of this effort has been the development of methodology capable of producing performance evaluation materials for volatile organics in water and soil which are truly blind, allowing a more relevant assessment of the precision and accuracy of the analytical methods.

The generation of a data base establishing preanalytical holding times presents formidable experimental difficulties, including the need for a large number of identical sample aliquots, the need for a variety of sample matrices, and the desire for a large number of potential analytes to be present. The high vapor pressure of these analytes requires that precautions be taken to minimize losses during sample aliquot preparation. In addition, since most environmental samples contain only a few of the potential analytes, a laboratory method for the preparation of samples containing all target compounds must be developed. Two criteria must be met by such samples: They should be "real", i.e., they should closely simulate the composition of actual samples; they should also be of defined stability. Fortunately, an analytical method gas chromatography/mass spectrometry (GC/MS), exists which is capable of determining all volatile analytes in a single run. However, there are analytical problems related to the long-term drift of the instrument, the stability of standard compounds, and the use of a method which was originally designed for screening purposes, not for highly accurate quantitative determinations. In

this work, these limitations have been largely overcome, and the data base reported here can be used to make an accurate assessment of the stability of volatile organic compounds in environmental water samples.

The initial results of the study indicated that most analytes were stable for a significant period of time. However, it was clear that preservation techniques could be developed which would eliminate most of the degradation which was encountered. Therefore, a follow on study was conducted on the merits of preservation. The results of that study are also reported here.

EXPERIMENTAL

The sample storage vials used were 40 mL borosilicate glass vials with teflon faced silicone septa and screw caps with holes purchased from Shamrock Glass Company (catalog number 6-06K). These vials were received fully assembled and pre-cleaned according to EPA 40 CFR 136 and EPA 40 CFR 141 regulations. Three water sample matrices were used for this study: reagent grade water (water 1), a ground water (water 2), and a surface water (water 3). Reagent grade water was obtained from Burdick and Jackson Laboratory. The ground water was drawn from Well #1 at the Oak Ridge National Laboratory (ORNL) Aquatic Ecology Facility (well depth: 205 feet; static water level below ground level: 30 feet). Surface water was taken from the headwaters of White Oak Creek. The methanol used was distilled-in-glass grade obtained from Burdick and Jackson Laboratory. All target compounds used were obtained either from the United States Environmental Protection Agency (USEPA) Quality Assurance Materials Bank (Research Triangle Park, NC) (2) or were of equivalent purity and obtained commercially. The following analytes were included in the study: methylene chloride; 1,1-dichloroethene; 1,1-dichloroethane; chloroform; carbon tetrachloride; 1,2-dichloropropane; trichloroethene; benzene; 1,1,2-trichloroethane; bromoform; 1,1,2,2-tetrachloroethane; tetrachloroethene; toluene; chlorobenzene; ethylbenzene; styrene; and o-xylene.

One-liter Tedlar air sampling bags with dual stainless steel fittings (hose/valve fitting and replaceable septum, catalog number 231-01) were obtained from SKC, Inc. The desired water was dispensed into a 1-liter Tedlar gas sampling bag. The water was allowed to degas for three days, and the gas was removed from the bag. Target compounds were received from the aforementioned sources as methanolic solutions of 1800 to 2300 μg volatiles/mL methanol. Appropriate volumes of each stock volatile organic solution were introduced through the septum port using gas tight syringes. The contents of the Tedlar bag were mixed thoroughly by hand agitation for three minutes after which the bags were allowed to sit for thirty minutes. After mixing, the sample was aliquotted into the 40 ml vials by gravity flow. Teflon tubing (¼" x 6") was used to allow the vial to be filled from the bottom up, preventing mixing of the water with air. Each bottle was completely filled with sample so that no headspace would remain after the bottle is sealed. Each bottle is sealed immediately with a Teflon faced septum and screw cap with hole, and stored at the appropriate temperature (4°C and 25°C). Blank samples were aliquotted prior to

addition of the stock volatile organic solutions. Blanks and samples were stored together in order to assess the possibility of cross contamination.

All volatile organic analyses were performed by gas chromatography with mass spectrometric detection (GC/MS) according to standard EPA Contract Laboratory Program (CLP) methods (3), except for the use of daily external standards (instead of internal standards) to calculate results. Data were used without recovery or blank correction, as is customary with this method. Samples of higher concentration were analyzed by addition of a 2 mL aliquot to the instrument rather than the customary 5 mL. This was done in order to maintain instrument response within the linear range of the instrument.

Samples preserved with hydrochloric acid were prepared by titrating each water matrix with 1N HCl until pH=2 before dispensing the waters into Tedlar bags. Samples preserved with sodium bisulfate or ascorbic acid were prepared by adding 0.25 g or 0.50 g respectively of the dry acid to each 40 mL vial prior to the addition of the spiked water sample. Measurements indicated the pH of samples preserved with sodium bisulfate (pK_a = 1.92) was 1.92 ± 0.04; the pH of samples preserved with ascorbic acid (pK_a = 4.1) was 2.98 ± 0.16.

The experimental factors for holding time study of volatile samples are:

FACTORS	LEVELS
1. Aqueous Solutions	Distilled Water, Ground Water, Surface Water
2. Contamination Level	Low Level (~50 μg/L), High Level (~500 μg/L)
3. Storage Temperature	None at day 0, 4°C, Room Temperature
4. Storage Time (Days)	0, 3, 4, 7, 14, 28, 56, 112, 365

The experimental design was a complete factorial design. For each combination of factor levels, 17 VOC were analyzed on four replicate samples. The total number of samples planned was 360 samples and the number of chemical analyses was 6,120 (i.e., 17 X 360 = 6,120).

Athough 6,120 chemical analyses were performed, about 5% of the high-level chemical analyses and about 11% of the low-level chemical analyses were delted as outliers from the data base. Potential outliers were first identified by comparing the change in the standard deviations among the days for each storage condition. Additional potential outliers were also identified by their large studentized residuals (e.g., > 2.5) for the zero-order and first-order regressions of concentrations vs storage times. An identified outlier value was rejected by examining the corresponding GC/MS data that indicated: (1) the

analysis resulted in an unusually low or high concentration, or (2) the analysis corresponded to an incorredt analysis of a reference standard, or (3) the analysis had been compromised by procedure problems.

RESULTS AND DISCUSSION

This study was designed to take into account as many variables as possible within the limitations of budget and sample capacity. Two concentration levels were used: 50 μg/L and 500 μg/L. Higher levels were not considered since it was expected that stability would improve with increasing concentration. Three matrices were chosen in order to assess the effect of varying water quality parameters on stability. The storage conditions were chosen based on the possibility that samples might not be continuously chilled during collection and storage. Time intervals were chosen on the basis of a logarithmic increase, but were also designed to bracket the existing holding time of 10 days (3).

Of primary importance to the conduct of this study was the ability to generate large numbers of identical aliquots of the sample. It was expected that mixing and aliquotting of the samples would take appreciable time and could create a bias in the concentration of the first aliquots versus the final aliquots. Therefore two possible methods were tested. In the first method, the water samples were added to the vials and the stock solutions added to each vial. In this case, variability in the concentrations found in each vial was 10-20%. In the second method, the stock solutions were added to a Tedlar gas sampling bag, mixed in the bag with no headspace, and added to the vials (4,5). This procedure produced concentration variability of less than 5%, and was therefore selected as the method of choice. Subsequent studies showed that the concentration of the compounds in the bag did not change over a 24-hour period.

The use of the Tedlar gas sampling bags provided several advantages. First, large volumes of sample could be prepared using minimal amounts of methanol. Second, vial to vial variability - considerable with individual spikes (Table 1) - was reduced. Third, the sample could be successfully stored in the bag (Table 2). Fourth, the accuracy of the concentration of the analytes in the sample was improved due to the larger volume of spiking solution relative to the very small volume needed to spike an individual vial. Finally, the bag allowed the filling of the individual sample vials with no introduction of headspace and minimal mixing of the aliquots with air during filling of the vials. Data from the analysis for seventeen volatile organic analytes added to three water samples on day zero of the sample preparation study is given in Table 3. With a few exceptions, the standard deviations from four replicates for each data point are approximately 10% or less of the mean value. Since it is useful to look at each individual water sample at a given concentration level to check the average of the data for all of the compounds, Table 3 also gives the average of the values for all compounds in this preliminary study for each water sample and concentration level. The target concentrations were 50 μg/L for the low concentration level and 500 μg/L for the high concentration level. Table 4 presents mean values derived by averaging the mean day zero results from all three water samples for a

TABLE 1

REPEATABILITY OF VOA SPIKING
INTO INDIVIDUAL VOA VIALS

(ug volatiles/L water)

COMPOUND	REP 1	REP 2	REP 3	MEAN	% Std Dev
Carbon Tetrachlroide	30	21	21	24.0	22
Chlorobenzene	29	20	19	22.7	24
1,1-Dichloroethane	30	20	20	23.3	25
1,1,2-Trichloroethane	35	25	23	27.7	23
Chloroform	27	18	19	21.3	23
1,1-Dichloroethene	33	22	22	25.7	25
1,2-Dichloropropane	34	24	24	27.3	21
Methylene Chloride	33	20	19	24.0	32
Chlorodibromomethane	27	18	17	20.7	27
Trichloroethene	17	12	12	13.7	21

TABLE 2

STABILITY OF AQUEOUS VOLATILES IN TEDLAR BAGS AT 4°C

MEAN CONCENTRATION LEVELS

COMPOUND	DAY 0		DAY 3	
	Mean (ug/L)	% Std Dev	Mean (ug/L)	% Std Dev
Carbon Tetrachloride	33.8	1.3	33.8	1.7
Chlorobenzene	32.5	1.0	33.3	1.0
1,1-Dichloroethane	34.3	1.5	30.0	1.7
1,1,2-Trichloroethane	45.8	1.5	52.0	5.0
Chloroform	52.3	1.5	84.0	2.6
1,1-Dichloroethene	29.8	2.2	26.3	2.0
1,2-Dichloropropane	41.5	2.1	45.8	1.7
Methylene Chloride	45.5	1.3	57.0	1.4
Chlorodibromomethane	42.3	1.5	47.8	2.2
Trichloroethene	22.3	1.3	28.0	0.0

TABLE 3

VOLATILE ORGANIC COMPOUNDS IN WATER SAMPLES
CONCENTRATIONS AS DETERMINED ON DAY ZERO

Compound	Water 1 Low level ug/L (n=4)		Water 1 High level ug/L (n=4)		Water 2 Low level ug/L (n=4)		Water 2 High level ug/L (n=4)		Water 3 Low level ug/L (n=4)		Water 3 High level ug/L (n=4)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Methylene chloride	53.1	3.5	464.1	31.3	66.4	1.5	396.1	111.3	69.9	3.7	544.0	38.8
1,1-Dichloroethene	57.6	3.2	472.9	17.5	61.3	1.7	383.4	121.1	53.2	4.6	408.9	61.3
1,1-Dichloroethane	63.9	2.7	514.7	18.1	66.2	1.6	388.6	111.3	64.7	3.4	593.8	59.5
Chloroform	59.6	1.8	488.8	25.0	61.0	1.4	385.5	114.3	69.5	4.1	570.3	46.7
Carbon tetrachloride	50.7	3.8	445.9	27.2	56.2	1.0	551.1	39.4	46.8	2.6	681.8	62.4
1,2-Dichloropropane	49.7	3.0	421.0	13.2	34.4	0.3	589.7	64.5	55.1	2.3	553.7	79.2
Trichloroethene	56.7	3.9	287.0	1.4	107.9	2.9	570.3	63.2	60.0	3.6	505.7	61.0
Benzene	49.6	2.7	400.2	11.1	54.6	0.2	569.7	50.2	55.5	2.3	479.7	34.7
1,1,2-Trichloroethane	47.3	1.7	440.5	17.8	55.4	1.0	584.4	74.9	59.4	2.1	649.5	150.1
Bromoform	33.9	3.5	619.3	47.2	49.6	0.1	583.3	77.9	54.8	2.2	766.1	178.2
1,1,2,2-Tetrachloroethane	41.8	1.3	531.3	49.1	48.5	6.0	544.0	36.5	54.2	5.5	797.3	127.1
Tetrachloroethene	49.8	3.1	369.7	19.1	52.6	1.7	530.6	40.5	57.0	4.3	398.1	47.4
Toluene	49.7	3.1	383.0	19.4	54.1	0.8	550.0	34.4	54.3	3.3	462.3	35.0
Chlorobenzene	51.6	2.6	381.7	21.7	55.4	1.1	547.4	36.5	55.9	3.6	476.9	33.9
Ethylbenzene	48.6	1.5	378.0	23.8	51.2	1.1	532.2	43.7	52.1	4.1	416.8	42.2
Styrene	52.5	2.4	394.1	24.4	63.3	1.8	535.2	41.2	57.7	3.5	486.1	28.7
O-Xylene	53.7	2.7	397.5	23.4	53.0	0.9	531.4	36.0	58.3	3.9	473.6	34.2
Mean (all compounds)	51.2		434.7		58.3		516.1		57.6		545.0	
Standard deviation (all compounds)	6.6		74.5		14.4		73.1		5.8		115.7	
% Standard deviation (all compounds)	12.8		17.1		24.8		14.2		10.0		21.2	

Water 1: Distilled Water Water 2: Ground water Water 3: Surface Water

TABLE 4

MEANS OF MEAN LOW AND HIGH CONCENTRATION LEVELS OF TARGET COMPOUNDS IN THREE WATER SAMPLES
LOW AND HIGH SPIKE LEVELS

	Low level ug/L (n=3)			High level ug/L (n=3)		
	Mean	SD	% SD	Mean	SD	% SD
Methylene chloride	63.1	7.2	11.5	468.1	60.5	12.9
1,1-Dichloroethene	57.4	3.3	5.8	421.7	37.7	8.9
1,1-Dichloroethane	64.9	0.9	1.4	499.0	84.5	16.9
Chloroform	63.4	4.4	6.9	481.5	75.6	15.7
Carbon tetrachloride	51.2	3.8	7.5	559.6	96.5	17.2
1,2-Dichloropropane	46.4	8.8	18.9	521.5	72.6	13.9
Trichloroethene	74.9	23.4	31.3	454.3	121.2	26.7
Benzene	53.2	2.6	4.9	483.2	69.2	14.3
1,1,2-Trichloroethane	54.0	5.0	9.3	558.1	87.3	15.6
Bromoform	46.1	8.9	19.3	656.2	79.1	12.0
1,1,2,2-Tetrachloroethane	48.1	5.1	10.5	624.2	122.5	19.6
Tetrachloroethene	53.1	3.0	5.6	432.8	70.1	16.2
Toluene	52.7	2.1	4.0	465.1	68.2	14.7
Chlorobenzene	54.3	1.9	3.5	468.7	67.9	14.5
Ethylbenzene	50.6	1.5	2.9	442.3	65.5	14.8
Styrene	57.8	4.4	7.7	471.8	58.5	12.4
O-Xylene	55.0	2.4	4.3	467.5	54.8	11.7

particular compound with a given target concentration. Tables 5 and 6 reference the EPA-CLP contract-required recovery limits for VOA surrogate and matrix spike compounds. These limits are a measure of expected reproducibility in the quantitative determination of volatile organics by GC/MS. The degree of reproducibility obtained with the methods of sample preparation and analysis presented in this paper is obviously high, relative to current standards.

The database generated by the sample stability study is formidable in size. Tables A.1 - B.17 and Figures A.1 - B.17 contain the summary data for all replicate anlayses and are included as part of the appendix. Significant trends in the data are displayed as figures and included in the body of this report. With the exception of 1,1,2,2-tetrachloroethane, all of the compounds included in this study were stable in distilled water for 24 days when samples were stored under refrigerated conditions. This was surprising in view of the limited holding times allowed for this type of sample. At room temperature, the tetrachloroethane disappeared very quickly with a concomitant rise in the concentration of trichloroethylene (Figure 1). This reaction also occurred at 4°C, although at a much slower rate. Likewise, a decrease in levels of trichloroethane was accompanied by increased concentrations of dichloroethylene in those samples stored at room temperature. These phenomena are most likely due to dehydrohalogenation reactions. Importantly, there seems to be no difference in the stability of the compounds based on volatility, which suggests that the current containers and storage conditions are quite adequate for the elimination of losses due to volatilization. The dependency of the holding times on analyte concentrations was complex. For example, for surface waters, the high concentration samples tended to have longer maximum holding times (MHT's) than the low concentration samples. For distilled water, the situation was reversed. For groundwater, there was no clear trend.

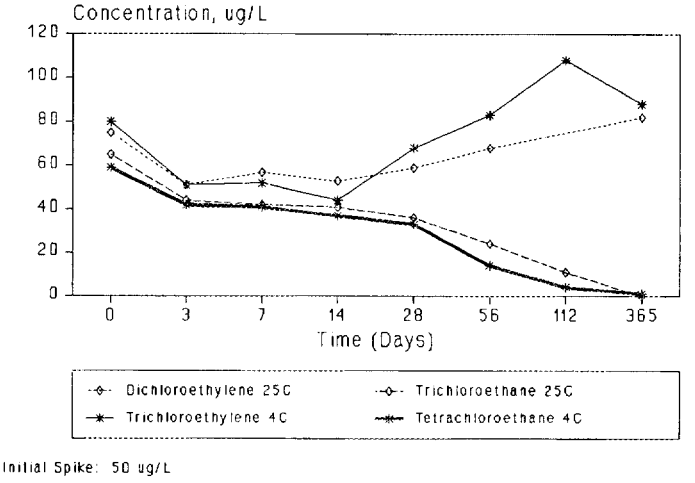


Figure 1. Dehydrohalogenation reactions in distilled water.

TABLE 5

RANGE OF CONTRACT REQUIRED SURROGATE SPIKE RECOVERY LIMITS
(Reference No. 3)

FRACTION	SURROGATE COMPOUND	% RECOVERY	
		WATER	LOW/MEDIUM SOIL
VOA	Toluene-d8	88-110	81-117
VOA	4-Bromofluorobenzene	86-115	74-121
VOA	1,2-Dichloroethane	76-114	70-121

TABLE 6

RANGE OF MATRIX SPIKE RECOVERY LIMITS
(Reference No. 3)

FRACTION	MATRIX SPIKE COMPOUND	% RECOVERY	
		WATER	LOW/MEDIUM SOIL
VOA	1,1-Dichloroethene	61-145	59-172
VOA	Trichloroethene	71-120	62-137
VOA	Chlorobenzene	75-130	60-133
VOA	Toluene	76-125	59-139
VOA	Benzene	76-127	66-142

In the case of the groundwater and surface water samples, both of which contained native chloride, no dehydrohalogenation was noted under refrigerated conditions (Figure 2). However, degradation of the aromatic volatiles was apparent by 28 days (Figure 3). It is not clear whether this is the result of chemical or microbial action, although both may play a part. The phenomenon was most pronounced with styrene and ethylbenzene, which are the most reactive of the aromatics. Since all samples were stored in the dark, it is unlikely that photodegradation occurred. The data also indicate gradual decreases in the measured concentrations of carbon tetrachloride in surface water samples. Day-to-day variations in these data are well within the range of GC/MS method variability, as demonstrated in Figure 4. The data for four EPA-CLP matrix spike compounds in ground water are shown relative to their contract-required recovery limits, and none fall outside the mandated range.

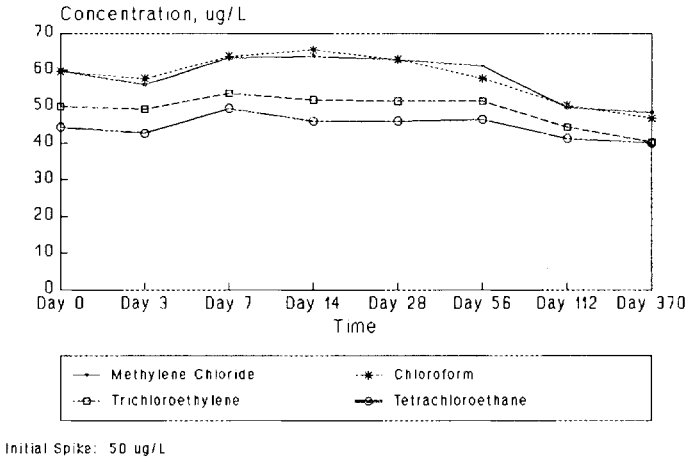


Figure 2. Stability of Chlorinated Hydrocarbons. Surface water stored at 4°C.

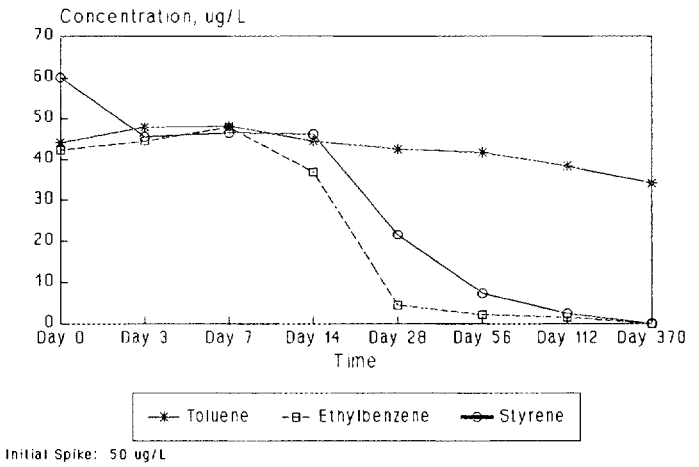


Figure 3. Stability of Aromatic Compounds. Surface water stored at 4°C.

Due to the nature of the changes which occurred in the course of this study, it became apparent that addition of hydrochloric acid to the samples, reducing the pH below 2, might inhibit both dehydrohalogenation and degradation of the aromatics. Therefore, a

second set of experiments was performed, using the same three water samples stored under refrigerated conditions and analyzed at intervals of 0, 14, 28, and 56 days. Tables C.1 - C.3 contain the data generated by these experiments and are included in the appendix to this report. No deterioration was noted in any of the compounds except styrene; moreover, the stability of styrene was greatly improved, with almost 80% remaining after 56 days. This study indicates that the maximum holding time of volatile organic compounds in water can be increased to at least 56 days if samples are preserved with hydrochloric acid. The significance of this increase to the environmental analytical laboratory cannot be over emphasized.

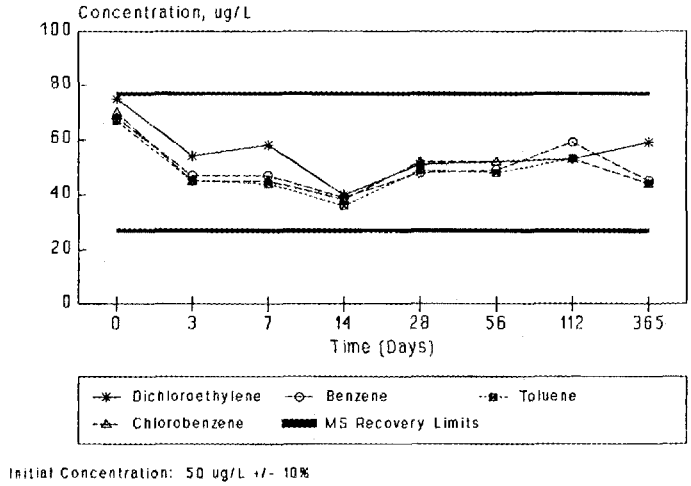


Figure 4. Stability of Matrix Spike Compounds in Ground Water.

Preservation of water samples with HCl has its drawbacks. It is difficult to ensure that the pH of the sample is reduced to 2 without first measuring sample pH. It is also inconvenient to add a corrosive liquid during field sampling. Finally, HCl does have appreciable volatility, and can be introduced into the instrumentation during purging. The possible detrimental effect on the analytical equipment cannot be tolerated. Therefore, there has been a general reluctance to require the use of HCl as a preservative for volatile organic compounds in water.

Because of these problems, and also because the database generated here indicated that pH reduction is the primary factor involved in preservation, an attempt was made to identify other acids which might have the preservative effect of HCl without the attendant drawbacks. Two candidates were identified: sodium bisulfate and ascorbic acid. Both are non-corrosive (in the dry form), readily available, inexpensive, and non-volatile. A study was carried out using these acids as preservatives, storing the samples at 4°C; the data generated was compared to that obtained without preservation and with HCl preservation (Appendix: Tables D.1 - E.3). Figure 5 shows the data for bisulfate preservation of ethylbenzene and styrene, two of the least stable aromatics. It is readily apparent that sodium bisulfate is as effective a preservative as HCl. Figure 6 illustrates the data obtained for five EPA target ketones. These compounds were not included in the original 365 day study because of difficulty in obtaining standard compounds. Gradual reductions in the levels of carbon disulfide were evident during the 112-day study; the other four

ketones remained at or near their original concentrations. Figure 7 depicts the ground water data for ketones in line graph format. Bolded lines again indicate EPA-CLP matrix spike recovery limits. One would expect greater variability from the more soluble ketones than from the more purgeable matrix spike compounds. However, virtually all the ketone data fall within matrix spike recovery limits.

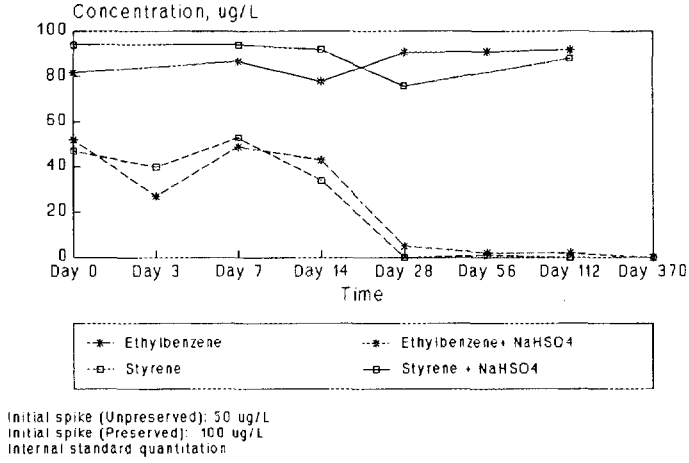


Figure 5. Bisulfate Preservation of Aromatics. *Surface Water Stored at 4°C.*

Ascorbic acid was equally effective in preserving most volatiles studied. However, it was not possible to acidify the samples to ph=2 with this acid, and solubility problems were encountered before reaching pH=3. Additionally, the quantitation of bromoform proved difficult in the presence of ascorbic acid, with high standard deviations between replicate samples.

Throughout this study, data obtained for the gases bromomethane and chloromethane were highly inconsistent due to instability of the standard compounds used for GC/MS quantitation. Aging of analytical standards is a problem that must be addressed before consistent data can be generated for these gases. Data on these compounds were deemed less useful and are not included in this report.

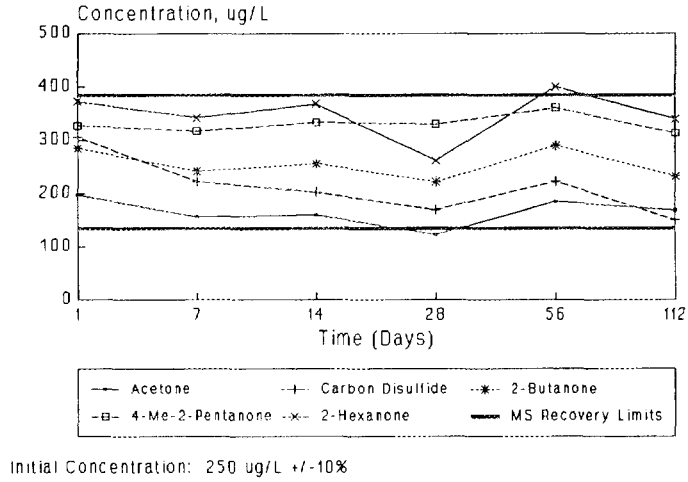


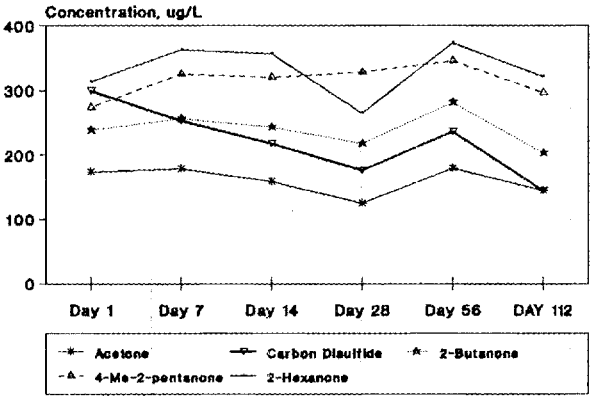
Figure 7. Ketones in Ground Water, Bisulfate Preservation.

Bisulfate Preservation of Ketones

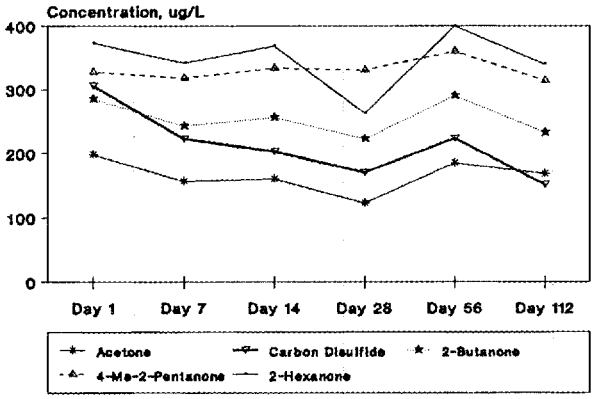
Initial Concentration: 250 ug/L

Storage at 4 C.

Distilled Water



Ground Water



Surface Water

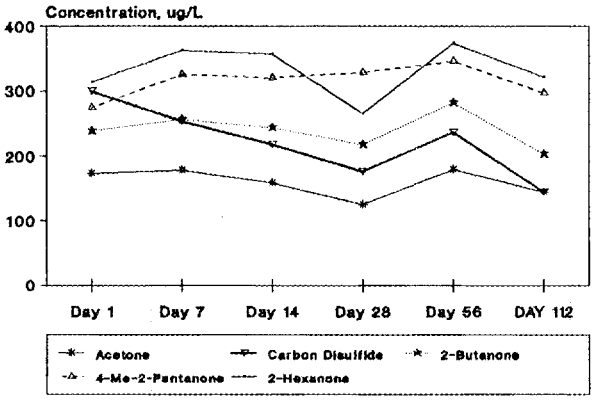


Figure 6

DETERMINATION OF MAXIMUM PRE-ANALYTICAL HOLDING TIMES BY STATISTICAL METHODS

The purpose of the work described herein was to determine the maximum length of time which a sample can be held without processing prior to analysis for a specific contaminant. One obvious criterion for "how long is too long" is the point in time where the concentration of the target constituent begins to fall outside the range of acceptability limits for the recovery of a matrix spike. However, the EPA CLP matrix spike recovery limit range can be so large that unacceptably large changes in target analyte concentration can occur without exceeding the range limits. Therefore, another approach was developed which established more stringent criteria for the concept of a pre-analytical holding time. These criteria were defined in terms of the point at which the measured sample concentration falls outside of the confidence interval boundaries of a mathematical approximation of the change in sample concentration with time. The two primary MHT definitions examined were those of the American Society for Testing and Materials and Environmental Science and Engineering, Inc. (ESE), the latter developed in cooperation with EPA's Environmental Monitoring and Support Laboratory.

Approximating Models

Maximum holding time (MHT) was defined as the maximum period of time during which a properly collected and stored sample can be stored before some degradation of the analyte occurs in the sample matrix. Calculating the MHT depends on the approximating model used to predict the expected concentration for any time during the experimental period (i.e., 365 days). Two approximating models were considered. One was based on zero-order kinetics and the other on first-order kinetics. The zero-order approximating model represents a constant change in the expected concentration with time. The first-order approximating model represents the change in the expected concentration with time which depends upon the concentration level. These two approximating models are expressed mathematically as:

Zero-Order Approximating Model:

$$dE(C)/dD = \beta,$$

or

$$E(C) = \quad + \beta D,$$

where

$dE(C)/dD$ = the change in the expected concentration (μg/L) with respect to time (D, days),

$E(C)$ = the expected concentration on a specified day,

= the intercept or concentration on day = 0,

β = the slope or change in the expected concentration per day.

First-Order Approximating Model:

$$dE(C)/dD = \beta C,$$

or

$$E(C) = \exp(\beta D),$$

or

$$\ln[E(C)] = \ln(\ ) + \beta D,$$

where

ln = the natural logarithm (i.e., base e),

β = the slope is now the change in the logarithm of the expected concentration per day.

The two unknown parameters and β are estimated from the holding time data using the method of least squares [8]. The method of least squares estimates the unknown parameters by minimizing the sum of squared differences between the observed concentrations and the predicted concentrations. The calculations to estimate the unknown parameters were made using the SAS [9] computer programming system. The estimated approximating models are:

Estimated Approximating Models:

$$\hat{C} = C_0 + bD \quad \text{(zero-order)},$$

$$\hat{C} = C_0\exp(bD) \quad \text{(first-order)},$$

where

$\hat{C}$ = the estimated expected concentration,

C_0 = the estimated concentration on day 0,

b = the estimated slope for either the expected concentration or the logarithm of the expected concentration.

The approximating model which had the smallest value for the sum of squares of the residuals (i.e., observed - predicted):

$$\Sigma(C - \hat{C})^2$$

was chosen to represent the behavior of the expected concentrations.

MHT Definition

The ASTM and the ESE definitions were used to calculate the MHT after choosing the approximating model for the expected concentrations. The ASTM definition [10] is described in volume 11.02 of the 1986 Annual Book of ASTM Standards. For the purposes of this study, the ASTM definition was applied as follows:

ASTM

1. Fit the appropriate approximating model to the holding time data by the method of least squares.

2. Estimated the intercept, C_0, and its standard deviation, S_0.

3. Calculate the upper and lower 99% confidence interval on the intercept (i.e. $C_0 \pm t(df,0.005)S_0$, where $t(df,0.005)$ is the 99.5 percentile point of the t-distribution with df = degrees of freedom and S_0 is the standard deviation of the intercept).

4. The MHT is the time at which the approximating model is equal to the value of the lower confidence limit on the intercept if the estimated slope is negative. For positive estimated slopes, the MHT is the time at which the approximating model is equal to the value of the upper confidence limit on the intercept. MHT can be calculated by:

$$MHT = t(df,0.005)S_0/|b|,$$

where

$|b|$ = absolute value of the slope.

5. Estimated MHT values greater than the time of the experimental study are set equal to MHT = 365.

This working definition differs slightly from the exact ASTM definition because this holding time study did not employ the same experimental design as recommended by ASTM. The differences between the two definitions are that confidence intervals on the intercepts are used rather than the confidence intervals on the mean of ten replicate concentrations measured on day 0 (it would not have been possible to make ten replicate analyses within one day by GC/MS). Also, the intercept and slope of the approximating models were estimated by the method of least squares rather than the "best graphical fit" of the average concentration for each day. Figure 8 is illustrates the ASTM method for estimating the MHT for methylene chloride preserved with sodium bisulfate in surface water.

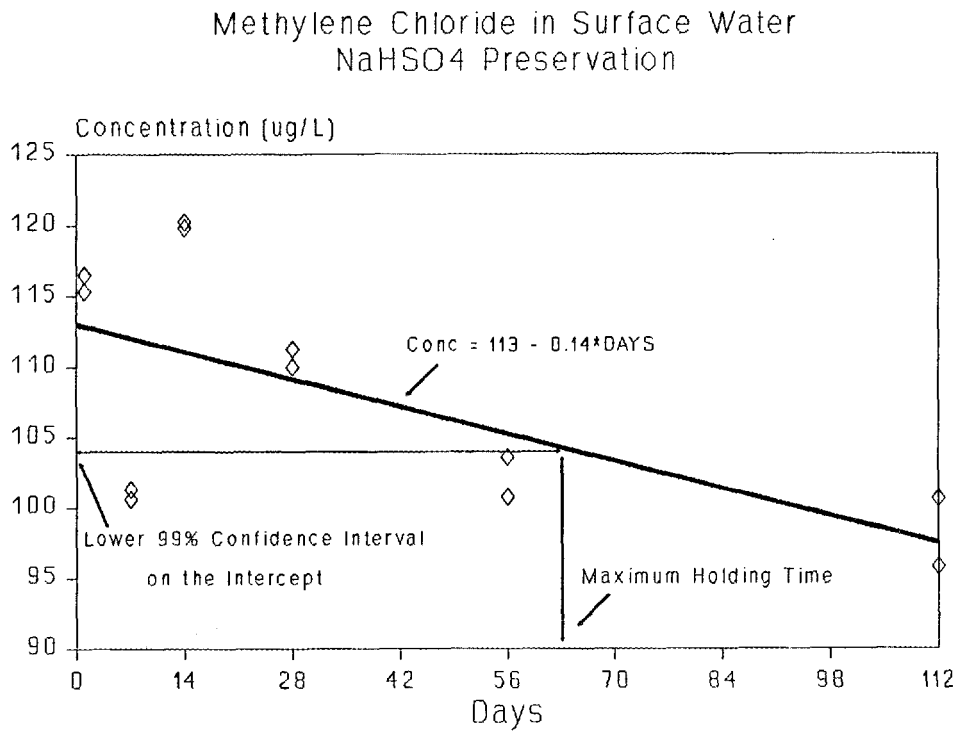


Figure 8. ASTM method for estimating maximum holding time.

A second definition for MHT was used in holding time studies on inorganic analytes conducted by Environmental Science and Engineering, Inc. (ESE) in cooperation with EPA's Environmental Monitoring and Support Laboratory [11]. The ESE definition is based on intersecting a 10% change in the intercept with a one-sided 90% confidence interval on the predicted concentration. Figure 9 is portrays the ESE method for estimating maximum holding times for the same case examined in Figure 8. For this holding time study, the ESE definition of MHT was applied as follows:

<u>ESE</u>

1. Fit the appropriate approximating model to the holding time data by the method of least squares.

2. Test that the slope is significantly different than zero with a two-sided t-test at 10% significance level (e.g., $|b| \geq t(df,0.05)S_1$, where t(df,0.05) is the 95 percentile point of the t-distribution with df = degrees of freedom and

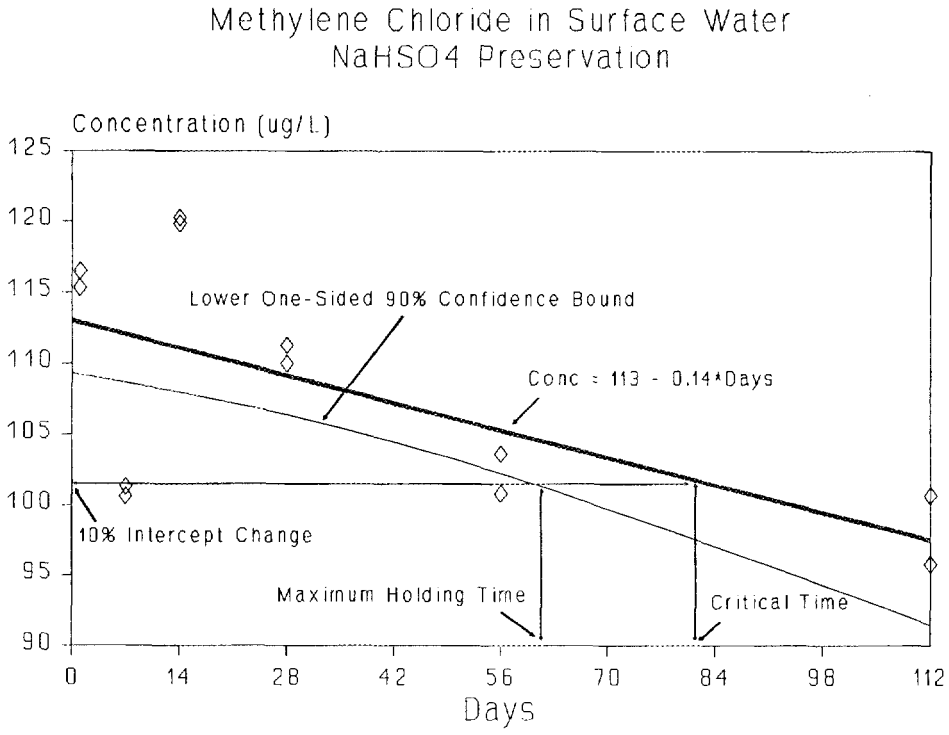


Figure 9. ESE method for estimating maximum holding time.

S_1 is the standard deviation of the slope). If the slope is not significantly different than zero then MHT = 365.

3. Construct a ± 10% interval about the intercept [e.g., (0.9C0, 1.1C0)]. Test that the 10% change is outside the 90% confidence interval on C_0 with a two-sided t-test at the 10% significance level [e.g., $0.1C_0 \geq t(df,0.05)S_0$ for zero-order, and $-\ln(.9) \geq t(df,0.05)S_0$ or $\ln(1.1) \geq t(df,0.05)S_0$ for first-order where t(df,0.05) is the 95 percentile point of the t-distribution with df = degrees of freedom and S_0 is the standard deviation of the intercept].

4. If a 10% change is not outside the 90% confidence interval, calculate the concentration change (i.e., $C_0 \pm KC_0$) that does occur outside the limits:

$K = t(df,0.05)S_0/C_0$ for zero-order,

$K = 1 - \exp[-t(df,0.05)S_0]$ for $b < 0$ and first-order, and

$K = \exp[t(df,0.05)S_0] - 1$ for $b > 0$ and first-order.

If $K > 0.15$, the two approximating models are usually not appropriate for estimating the expected concentrations. The MHT can't be estimated with these models and other approximating models must be investigated. However, large variability in the data may also cause $K > 0.15$.

5. Calculate the critical time (C_T) when the predicted concentration line intersects the significant concentration change ($0.10 \leq K \leq 0.15$) by:

$C_T = KC_0/|b|$ for zero-order,

$C_T = \ln(1 - K)/b$ for $b < 0$ and first-order, and

$C_T = \ln(1 + K)/b$ for $b > 0$ and first-order.

6. The MHT is defined as the one-sided lower 90% confidence interval on CT and can be calculated by:

$$MHT = C_T - t(df,0.10)[Var(C_T)]^{1/2},$$

where,

$t(df,0.10)$ = the 90 percentile point of the t-distribution, and

$Var(C_T)$ = the variance of C_T approximated by:

$$Var(C_T) = C_T^2[Var(C_0)/C_0^2 + Var(b)/b^2 - 2Cov(C_0,b)/bC_0].$$

with Var, and Cov indicating estimated variance and covariance, respectively.

The one-sided lower 90% confidence interval on C_T is equivalent to the day the one-sided lower(upper) 90% confidence interval on the predicted concentration has the value $C_0 \pm KC_0$. For this equivalent definition, the MHT is the smallest solution to a quadratic equation:

$$A(MHT)^2 + B(MHT) + C = 0, \text{ so}$$

$$MHT = -(B/2A) - [B^2 - 4AC]^{1/2}/2A.$$

The coefficients for the two approximating models are:

zero-order: $A = b^2 - t^2(df,0.10)Var(b)$,

$B = -2[|b|KC_0 + t^2(df,0.10)Cov(C_0,b)]$, and

$C = (KC_0)^2 - t^2(df,0.10)Var(C_0)$.

first-order: $A = b^2 - t^2(df,0.10)Var(b)$,

$B = -2[bG + t^2(df,0.10)Cov(C_0,b)]$, and

$C = G^2 - t^2(df,0.10)Var(C_0)$.

Where,

$G = \ln(1 + bK/|b|)$.

7. Estimated MHT values greater than the time of the experimental study are set equal to MHT = 365.

The MHT values using the ASTM definition and the ESE definition are given in Table 7 for high-level VOC and in Table 8 for low-level VOC. In addition, the estimated values of C_0 and the slope are given for the zero-order and first-order approximating models which were used to calculate the MHT values. The two models are identified by expressing the slope for the zero-order model as a number with four decimal places (e.g., 0.1649) and by expressing the slope for the first-order model as a number in exponential notation (e.g., -8.256E-04). The different values of MHT for the ASTM and ESE definitions depend on the variability of the data. This variability ultimately affects the width of the 99% confidence interval of the ASTM definition, but does not affect the 10% intercept change of the ESE definition. Therefore, when variability is high, the confidence interval will be broader than the 10% change. When variability is low, the confidence interval will be narrower than the 10% change.

Comparing the MHT values for samples preserved with the two acids, the results show that neither of the two acids is uniformly better for all analytes. For example using both definitions of MHT, the ascorbic acid MHT values are always higher for methylene chloride while the sodium bisulfate MHT values are always higher for trichloroethene, benzene, 1,1,2-trichloroethane, 4-methyl-2-pentanone, 2-hexanone, 1,1,2,2,-tetrachloroethane, tetrachloroethene, toluene, chlorobenzene, ethylbenzene and styrene. For other analytes, the stability of the analyte appears to depend on the type of water matrix. In general, the MHT values for sodium bisulfate preservation are higher than the MHT values for ascorbic acid preservation. For a particular analyte and water sample, the MHT values for ascorbic acid preservation may be higher.

Table 7. Estimated MHT days for high-level concentrations. First-order approximating models have slope values expressed in exponential notation.

Volatile Organic Compound	Water	Storage Temp.	CO	b	ASTM MHT	ESE MHT
Methylene Chloride	Distilled	4 C	441	0.1649	147	187
Methylene Chloride	Distilled	Room	447	-0.3122	86	108
Methylene Chloride	Ground	4 C	466	-0.2076	210	131
Methylene Chloride	Ground	Room	441	-0.2378	219	97
Methylene Chloride	Surface	4 C	489	-0.1126	203	273
Methylene Chloride	Surface	Room	491	-0.3494	118	91
1,1-Dichloroethylene	Distilled	4 C	415	0.2086	148	133
1,1-Dichloroethylene	Distilled	Room	474	-0.8453	61	30
1,1-Dichloroethylene	Ground	4 C	487	-8.256E-04	103	86
1,1-Dichloroethylene	Ground	Room	440	-1.660E-03	71	33
1,1-Dichloroethylene	Surface	4 C	459	-0.0808	365	365
1,1-Dichloroethylene	Surface	Room	440	-0.8991	49	28
1,1-Dichloroethane	Distilled	4 C	497	0.1760	183	184
1,1-Dichloroethane	Distilled	Room	470	0.0360	365	365
1,1-Dichloroethane	Ground	4 C	553	-0.2092	183	170
1,1-Dichloroethane	Ground	Room	517	-0.2002	220	154
1,1-Dichloroethane	Surface	4 C	536	0.0136	365	365
1,1-Dichloroethane	Surface	Room	518	-0.1214	365	365
Chloroform	Distilled	4 C	434	0.1716	131	183
Chloroform	Distilled	Room	411	-0.1861	142	153
Chloroform	Ground	4 C	501	-3.776E-04	169	186
Chloroform	Ground	Room	467	-0.1559	225	180
Chloroform	Surface	4 C	504	0.0149	365	365
Chloroform	Surface	Room	479	-0.0181	365	365
Carbon Tetrachloride	Distilled	4 C	436	-0.0061	365	365
Carbon Tetrachloride	Distilled	Room	378	-8.084E-04	122	82
Carbon Tetrachloride	Ground	4 C	478	-0.2325	274	365
Carbon Tetrachloride	Ground	Room	424	-0.2737	244	365
Carbon Tetrachloride	Surface	4 C	486	-0.2383	181	125
Carbon Tetrachloride	Surface	Room	469	-6.229E-03	43	7
1,2-Dichloropropane	Distilled	4 C	400	0.2999	102	92
1,2-Dichloropropane	Distilled	Room	368	0.2561	130	91
1,2-Dichloropropane	Ground	4 C	459	-0.0567	365	365
1,2-Dichloropropane	Ground	Room	427	-0.0155	365	365
1,2-Dichloropropane	Surface	4 C	441	0.2200	131	140
1,2-Dichloropropane	Surface	Room	429	0.0986	365	365

Table 7. (continued)

Volatile Organic Compound	Water	Storage Temp.	CO	b	ASTM MHT	ESE MHT
Trichloroethylene	Distilled	4 C	506	0.6191	124	28
Trichloroethylene	Distilled	Room	491	-1.1449	51	21
Trichloroethylene	Ground	4 C	462	-0.1720	202	166
Trichloroethylene	Ground	Room	478	-0.4930	98	57
Trichloroethylene	Surface	4 C	437	-0.0100	365	365
Trichloroethylene	Surface	Room	464	-0.5704	114	33
Benzene	Distilled	4 C	376	0.1762	140	148
Benzene	Distilled	Room	344	-0.1922	151	115
Benzene	Ground	4 C	429	-4.880E-04	145	148
Benzene	Ground	Room	397	-0.2335	172	100
Benzene	Surface	4 C	411	0.1387	217	180
Benzene	Surface	Room	394	-0.1725	282	365
1,1,2-Trichloroethane	Distilled	4 C	424	0.1609	183	171
1,1,2-Trichloroethane	Distilled	Room	(a)	(a)	(a)	(a)
1,1,2-Trichloroethane	Ground	4 C	491	-0.0415	365	365
1,1,2-Trichloroethane	Ground	Room	467	-7.264E-04	84	110
1,1,2-Trichloroethane	Surface	4 C	491	0.1488	231	365
1,1,2-Trichloroethane	Surface	Room	485	0.0210	365	365
Bromoform	Distilled	4 C	551	0.1797	212	190
Bromoform	Distilled	Room	506	-1.091E-03	88	61
Bromoform	Ground	4 C	599	-0.0408	365	365
Bromoform	Ground	Room	553	0.0131	365	365
Bromoform	Surface	4 C	601	0.1665	238	365
Bromoform	Surface	Room	583	-0.4622	143	68
1,1,2,2-Tetrachloroethane	Distilled	4 C	(a)	(a)	(a)	(a)
1,1,2,2-Tetrachloroethane	Distilled	Room	(a)	(a)	(a)	(a)
1,1,2,2-Tetrachloroethane	Ground	4 C	608	-0.1716	265	365
1,1,2,2-Tetrachloroethane	Ground	Room	520	-1.677E-02	7	3
1,1,2,2-Tetrachloroethane	Surface	4 C	583	0.1507	330	365
1,1,2,2-Tetrachloroethane	Surface	Room	477	-6.042E-03	36	5
Tetrachloroethylene	Distilled	4 C	300	-7.402E-04	126	92
Tetrachloroethylene	Distilled	Room	265	-9.186E-03	22	3
Tetrachloroethylene	Ground	4 C	288	-1.180E-03	78	58
Tetrachloroethylene	Ground	Room	230	-3.659E-03	40	11
Tetrachloroethylene	Surface	4 C	330	-8.329E-04	86	92
Tetrachloroethylene	Surface	Room	290	-4.762E-03	34	7

Table 7. (continued)

Volatile Organic Compound	Water	Storage Temp.	CO	b	ASTM MHT	ESE MHT
Toluene	Distilled	4 C	339	0.0960	288	365
Toluene	Distilled	Room	298	-0.4202	72	41
Toluene	Ground	4 C	394	-0.1646	188	152
Toluene	Ground	Room	322	-8.803E-04	145	62
Toluene	Surface	4 C	373	-9.096E-04	75	86
Toluene	Surface	Room	352	-0.3857	120	41
Chlorobenzene	Distilled	4 C	329	0.0926	307	365
Chlorobenzene	Distilled	Room	291	-2.624E-03	46	20
Chlorobenzene	Ground	4 C	392	-0.0770	365	365
Chlorobenzene	Ground	Room	333	-9.409E-04	125	62
Chlorobenzene	Surface	4 C	376	0.0261	365	365
Chlorobenzene	Surface	Room	344	-0.3615	134	39
Ethylbenzene	Distilled	4 C	311	0.0103	365	365
Ethylbenzene	Distilled	Room	261	-2.483E-03	52	19
Ethylbenzene	Ground	4 C	363	-0.1646	179	140
Ethylbenzene	Ground	Room	298	-2.500E-03	65	13
Ethylbenzene	Surface	4 C	(a)	(a)	(a)	(a)
Ethylbenzene	Surface	Room	279	-0.3627	117	27
Styrene	Distilled	4 C	326	0.0414	365	365
Styrene	Distilled	Room	280	-2.799E-03	48	16
Styrene	Ground	4 C	378	-0.0996	365	365
Styrene	Ground	Room	310	-2.571E-03	77	12
Styrene	Surface	4 C	342	-1.146E-03	82	59
Styrene	Surface	Room	314	-0.8746	54	11
o-Xylene	Distilled	4 C	334	0.0043	365	365
o-Xylene	Distilled	Room	277	-1.212E-03	102	45
o-Xylene	Ground	4 C	384	-0.0778	365	365
o-Xylene	Ground	Room	320	-2.083E-03	70	20
o-Xylene	Surface	4 C	361	0.0377	365	365
o-Xylene	Surface	Room	324	-0.1654	272	365

(a) Both the zero-order and first-order approximating models gave inappropriate results.

Table 8. Estimated MHT days for low-level concentrations. First-order approximating models have slope values expressed in exponential notation.

Volatile Organic Compound	Water	Storage Temp.	CO	b	ASTM MHT	ESE MHT
Methylene Chloride	Distilled	4 C	56	-0.0109	365	365
Methylene Chloride	Distilled	Room	57	-0.0183	199	197
Methylene Chloride	Ground	4 C	60	0.0160	189	252
Methylene Chloride	Ground	Room	58	-0.0018	365	365
Methylene Chloride	Surface	4 C	61	-6.848E-04	63	126
Methylene Chloride	Surface	Room	59	-6.491E-04	84	125
1,1-Dichloroethylene	Distilled	4 C	56	0.0062	365	365
1,1-Dichloroethylene	Distilled	Room	60	0.0617	93	58
1,1-Dichloroethylene	Ground	4 C	61	0.0098	225	365
1,1-Dichloroethylene	Ground	Room	60	-0.0385	151	99
1,1-Dichloroethylene	Surface	4 C	54	-9.650E-04	70	81
1,1-Dichloroethylene	Surface	Room	50	-1.149E-03	61	67
1,1-Dichloroethane	Distilled	4 C	63	-0.0219	252	365
1,1-Dichloroethane	Distilled	Room	62	-0.0237	237	365
1,1-Dichloroethane	Ground	4 C	67	0.0054	365	365
1,1-Dichloroethane	Ground	Room	64	-0.0049	365	365
1,1-Dichloroethane	Surface	4 C	58	-8.342E-04	48	106
1,1-Dichloroethane	Surface	Room	55	-5.607E-04	74	152
Chloroform	Distilled	4 C	61	-0.0265	202	145
Chloroform	Distilled	Room	59	-0.0376	134	101
Chloroform	Ground	4 C	62	0.0100	365	365
Chloroform	Ground	Room	57	0.0216	155	186
Chloroform	Surface	4 C	61	-8.052E-04	51	110
Chloroform	Surface	Room	59	-0.0135	160	303
Carbon Tetrachloride	Distilled	4 C	51	-0.0069	365	365
Carbon Tetrachloride	Distilled	Room	50	-0.0163	356	365
Carbon Tetrachloride	Ground	4 C	59	-0.0039	365	365
Carbon Tetrachloride	Ground	Room	55	-0.0426	138	76
Carbon Tetrachloride	Surface	4 C	47	-0.0312	84	115
Carbon Tetrachloride	Surface	Room	(a)	(a)	(a)	(a)
1,2-Dichloropropane	Distilled	4 C	52	-0.0066	365	365
1,2-Dichloropropane	Distilled	Room	51	-0.0085	365	365
1,2-Dichloropropane	Ground	4 C	47	0.0470	86	66
1,2-Dichloropropane	Ground	Room	44	0.0344	130	78
1,2-Dichloropropane	Surface	4 C	47	-3.561E-04	75	243
1,2-Dichloropropane	Surface	Room	45	-0.0043	365	365

Table 8. (continued)

Volatile Organic Compound	Water	Storage Temp.	CO	b	ASTM MHT	ESE MHT
Trichloroethylene	Distilled	4 C	65	0.0926	133	24
Trichloroethylene	Distilled	Room	82	-0.0327	180	162
Trichloroethylene	Ground	4 C	100	0.0199	301	365
Trichloroethylene	Ground	Room	104	0.0236	365	365
Trichloroethylene	Surface	4 C	51	-6.898E-04	47	132
Trichloroethylene	Surface	Room	53	0.0250	161	138
Benzene	Distilled	4 C	51	-0.0123	365	365
Benzene	Distilled	Room	50	-0.0161	324	365
Benzene	Ground	4 C	47	-1.431E-03	97	32
Benzene	Ground	Room	48	-0.0286	169	101
Benzene	Surface	4 C	48	-8.388E-04	55	103
Benzene	Surface	Room	43	-7.829E-04	76	100
1,1,2-Trichloroethane	Distilled	4 C	51	-0.0169	278	365
1,1,2-Trichloroethane	Distilled	Room	51	-1.348E-02	7	4
1,1,2-Trichloroethane	Ground	4 C	51	0.0419	42	105
1,1,2-Trichloroethane	Ground	Room	50	0.0268	104	144
1,1,2-Trichloroethane	Surface	4 C	49	-4.027E-04	77	214
1,1,2-Trichloroethane	Surface	Room	48	-2.813E-04	149	259
Bromoform	Distilled	4 C	40	0.0159	288	365
Bromoform	Distilled	Room	40	-0.0388	132	49
Bromoform	Ground	4 C	49	0.0375	81	99
Bromoform	Ground	Room	49	-0.0577	86	51
Bromoform	Surface	4 C	47	-7.094E-04	45	129
Bromoform	Surface	Room	44	-2.255E-03	23	37
1,1,2,2-Tetrachloroethane	Distilled	4 C	(a)	(a)	(a)	(a)
1,1,2,2-Tetrachloroethane	Distilled	Room	(a)	(a)	(a)	(a)
1,1,2,2-Tetrachloroethane	Ground	4 C	49	0.0396	83	91
1,1,2,2-Tetrachloroethane	Ground	Room	48	-1.131E-02	14	3
1,1,2,2-Tetrachloroethane	Surface	4 C	46	-0.0168	165	184
1,1,2,2-Tetrachloroethane	Surface	Room	38	-1.032E-02	10	6
Tetrachloroethylene	Distilled	4 C	48	-0.0181	365	365
Tetrachloroethylene	Distilled	Room	45	-0.0535	119	34
Tetrachloroethylene	Ground	4 C	46	0.0042	365	365
Tetrachloroethylene	Ground	Room	42	-0.0253	203	87
Tetrachloroethylene	Surface	4 C	46	-1.012E-03	49	84
Tetrachloroethylene	Surface	Room	39	-1.098E-03	74	66

Table 8. (continued)

Volatile Organic Compound	Water	Storage Temp.	C0	b	ASTM MHT	ESE MHT
Toluene	Distilled	4 C	49	-0.0109	365	365
Toluene	Distilled	Room	48	-0.0235	218	112
Toluene	Ground	4 C	42	-3.119E-03	62	10
Toluene	Ground	Room	42	-0.1026	49	20
Toluene	Surface	4 C	45	-8.448E-04	50	104
Toluene	Surface	Room	41	-0.0955	26	32
Chlorobenzene	Distilled	4 C	51	-0.0159	358	365
Chlorobenzene	Distilled	Room	49	-0.0291	197	90
Chlorobenzene	Ground	4 C	49	-0.0038	365	365
Chlorobenzene	Ground	Room	44	-0.0373	134	65
Chlorobenzene	Surface	4 C	45	-6.696E-04	57	132
Chlorobenzene	Surface	Room	40	-0.0218	104	129
Ethylbenzene	Distilled	4 C	47	-0.0142	365	365
Ethylbenzene	Distilled	Room	46	-0.0272	218	80
Ethylbenzene	Ground	4 C	(a)	(a)	(a)	(a)
Ethylbenzene	Ground	Room	32	-8.588E-03	32	5
Ethylbenzene	Surface	4 C	(a)	(a)	(a)	(a)
Ethylbenzene	Surface	Room	30	-0.0816	46	16
Styrene	Distilled	4 C	49	-0.0267	248	365
Styrene	Distilled	Room	48	-0.0415	155	52
Styrene	Ground	4 C	(a)	(a)	(a)	(a)
Styrene	Ground	Room	56	-7.898E-02	3	0
Styrene	Surface	4 C	(a)	(a)	(a)	(a)
Styrene	Surface	Room	(a)	(a)	(a)	(a)
o-Xylene	Distilled	4 C	51	-0.0197	310	365
o-Xylene	Distilled	Room	50	-0.0278	217	91
o-Xylene	Ground	4 C	40	-0.1255	74	12
o-Xylene	Ground	Room	40	-9.689E-03	19	3
o-Xylene	Surface	4 C	45	-6.689E-04	118	108
o-Xylene	Surface	Room	43	-0.1145	29	25

(a) Both the zero-order and first-order approximating models gave inappropriate results.

The addition of ascorbic acid or sodium bisulfate did not necessarily reduce the variability of the concentration measurements. Comparison of the standard deviations of analyses of samples with and without acid preservation, (estimated as the square root of the mean square error for either the zero-order or first-order model) indicated that the variability for the unpreserved samples are usually less than that for the preserved samples for ground and surface water but not for distilled water. The variability for preserved samples usually occurred in ground water samples, while the largest variability for unpreserved samples usually occurred in distilled water.

The MHT values identified by (a) in Tables 7 and 8 indicate that neither the zero-order or first-order approximating models gave appropriate results. These represent 12 of the 204 unpreserved cases and 2 of the 150 preserved cases. The difficulty with fitting the 12 unpreserved cases is that the concentrations decreased rapidly with time to a non-zero level after an initial period of apparent stability. A number of models were investigated in an attempt to fit the data. These are discussed more completely in Appendix F. The best approximation was obtained with a cubic spline equation between the initial and final concentrations. A cubic spline is a cubic polynomial with a sigmoidal shaped curve. Cubic splines were also used to fit the two acid preserved cases. Such an approach proved successful for all cases except for carbon tetrachloride in distilled water preserved with ascorbic acid. In that case, obvious boundaries for the MHT could be estimated graphically. A more detailed discussion of the use of the cubic spline is provided in Appendix F, along with the MHT's calculated using that approach.

From the results of these statistical analyses, it can be shown that each analyte has a MHT which can be established. Obviously, these are not related to the administrative/political aspects of the environmental analysis. Therefore, it is necessary to consider the end use of the data when determining the maximum holding time.

CONCLUSIONS

From a regulatory point of view, extension of sample holding times without compromising data quality would reduce the cost associated with waste site characterization and remedial action by reducing the possibility that additional sampling will be required due to the failure to meet the holding times. This has an important economic effect on investigations carried out under SARA. From the point of view of RCRA, where quarterly groundwater monitoring is carried out, preservation of the samples would allow direct comparison with the samples collected during the subsequent quarter. Since regulatory decisions are made based on changes in the groundwater concentrations of contaminants, this would be important in reducing analytical variability. From the standpoint of the regulated community, the ability to preserve and archive important samples for later verification would greatly reduce the possibility of error in regulatory decision-making, and would certainly eliminate the need for resampling.

From the analytical standpoint, improvements in the quality assurance process are expected. This study has shown that most of the volatile organics of interest are stable in water at refrigerator temperature for a time sufficient to allow distribution and analysis. Thus for the first time, stable, long-term performance evaluation materials can be prepared and submitted in a truly blind fashion to participating analytical laboratories. Studies of interlaboratory performance of this method can now be performed. Controls can also be prepared for use in field sampling. Finally, an estimate of the intralaboratory variability in the analytical method over long periods of time is now possible.

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Appendix A

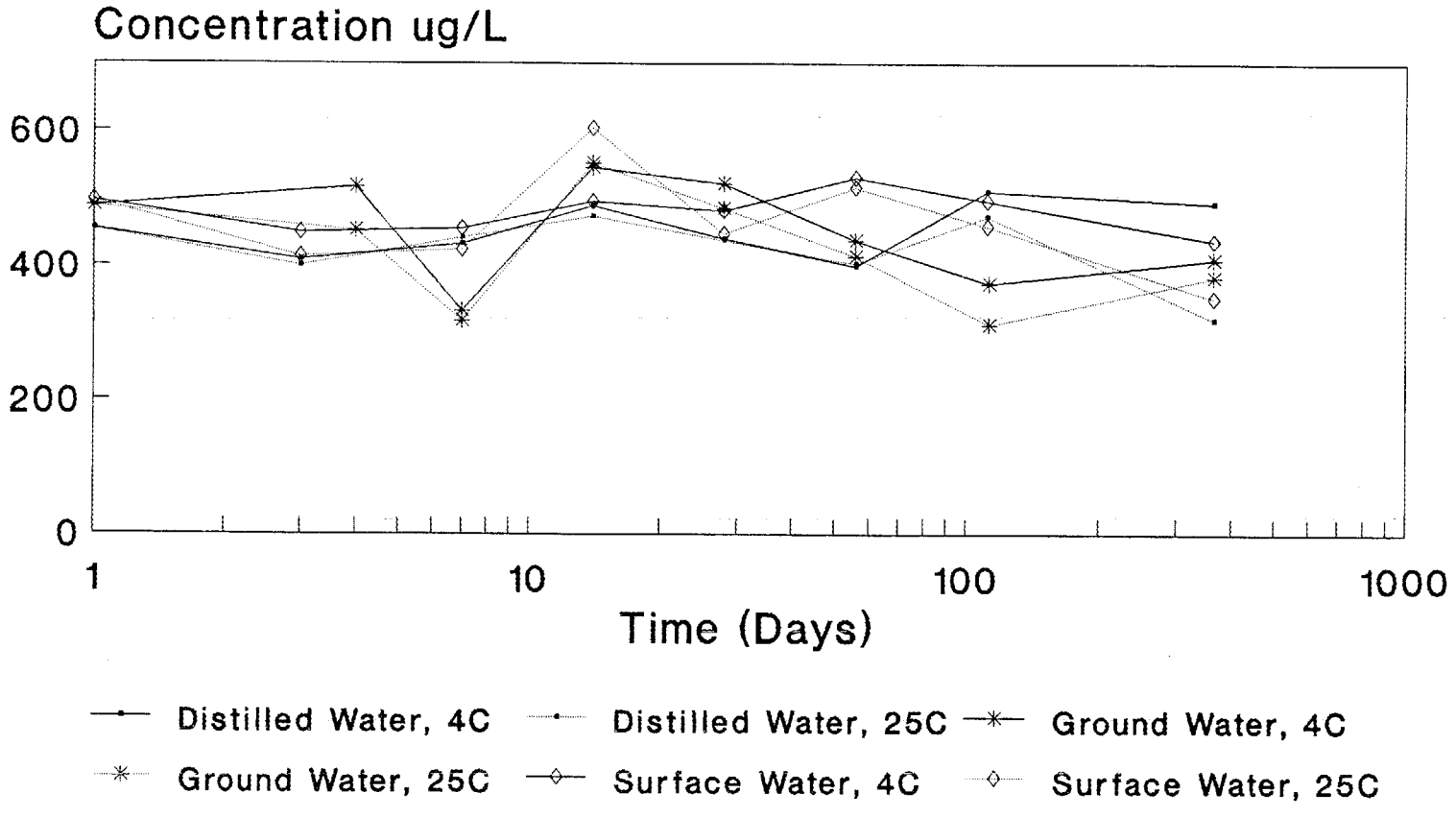
Data for Individual Volatile Organic Compounds

(High Concentration Level)

Table A.1 Summary Statistics for high level concentrations (μg/L) for Methylene Chloride.

Water	Storage Conditions		Days 0	3	4	7	14	28	56	112	113	365	All
Distilled	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	454	.	.	.	.	.	.	.	.	.	454
		St Dev	33	.	.	.	.	.	.	.	.	.	33
	4 C	Num	.	4	.	4	4	3	4	4	.	4	27
		Mean	.	409	.	432	489	440	399	511	.	492	454
		St Dev	.	9	.	39	10	11	14	22	.	22	46
	Room	Num	.	4	.	4	4	4	4	4	.	4	28
		Mean	.	400	.	441	473	437	403	473	.	319	421
		St Dev	.	19	.	20	41	20	59	34	.	42	60
Ground	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	488	.	.	.	.	.	.	.	.	.	488
		St Dev	33	.	.	.	.	.	.	.	.	.	33
	4 C	Num	.	.	3	4	4	4	4	.	4	4	27
		Mean	.	.	517	332	545	522	437	.	373	409	445
		St Dev	.	.	14	11	16	14	4	.	55	12	80
	Room	Num	.	.	3	4	4	3	4	.	4	4	26
		Mean	.	.	452	317	552	485	414	.	312	382	412
		St Dev	.	.	93	26	8	34	22	.	48	17	92
Surface	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	496	.	.	.	.	.	.	.	.	.	496
		St Dev	11	.	.	.	.	.	.	.	.	.	11
	4 C	Num	.	4	.	3	4	4	4	4	.	4	27
		Mean	.	449	.	455	495	481	531	496	.	436	478
		St Dev	.	29	.	25	48	12	30	29	.	44	43
	Room	Num	.	4	.	4	4	3	4	4	.	3	26
		Mean	.	414	.	424	604	447	516	458	.	351	464
		St Dev	.	33	.	66	25	36	34	33	.	16	83

Stability of Methylene Chloride in Environmental Water Samples



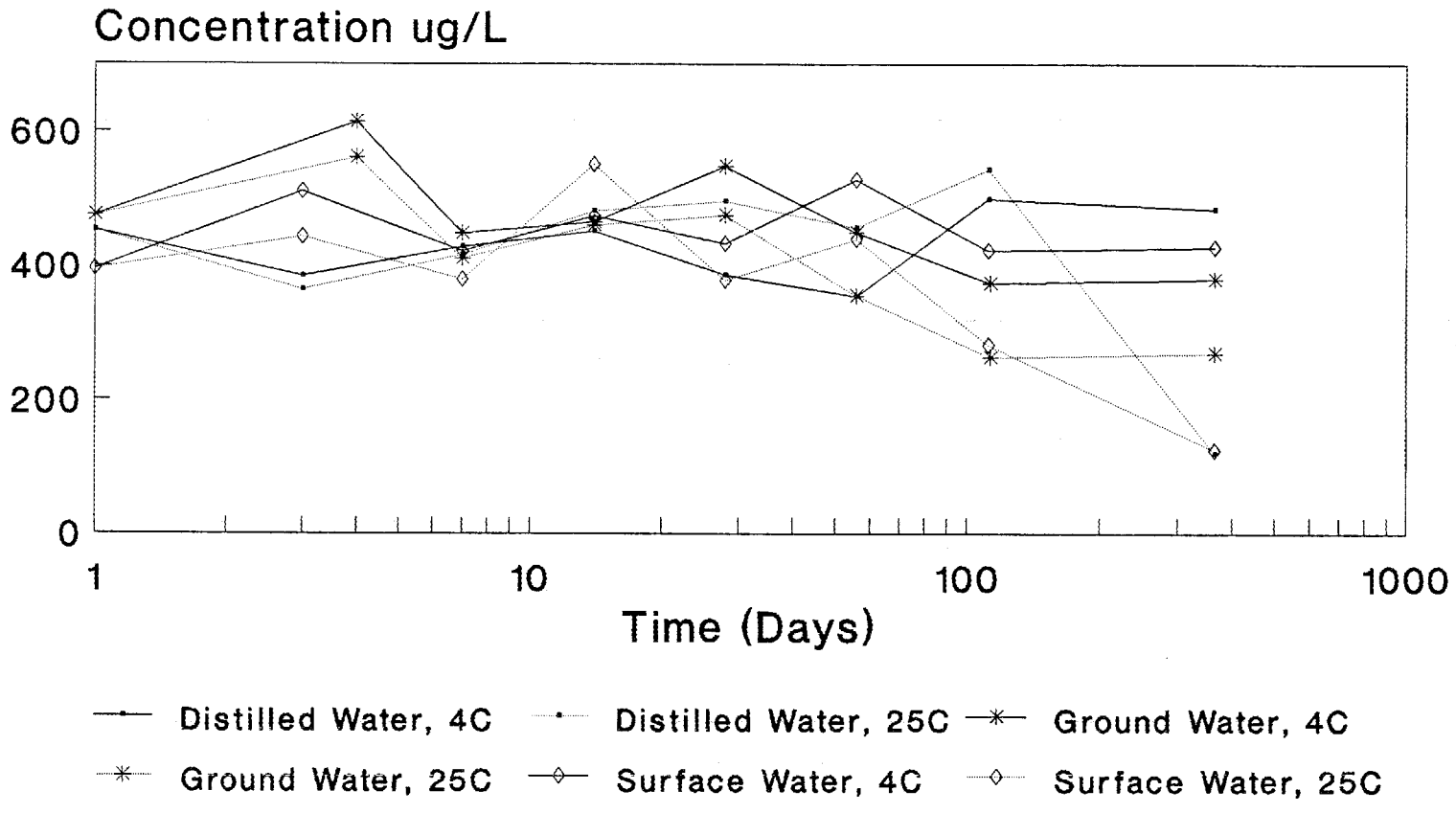
Initial Spike: 500 ug/L

Figure A.1

Table A.2 Summary Statistics for high level concentrations (μg/L) for 1,1-Dichloroethylene.

Water	Storage Conditions		Days 0	3	4	7	14	28	56	112	113	365	All
Distilled	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	453	.	.	.	.	.	.	.	.	.	453
		St Dev	23	.	.	.	.	.	.	.	.	.	23
	4 C	Num	.	4	.	4	4	3	4	4	.	4	27
		Mean	.	384	.	428	451	386	354	500	.	484	428
		St Dev	.	6	.	32	5	12	20	29	.	64	59
	Room	Num	.	4	.	4	4	4	4	3	.	4	27
		Mean	.	364	.	416	481	496	457	544	.	120	406
		St Dev	.	29	.	40	45	23	40	73	.	81	140
Ground	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	475	.	.	.	.	.	.	.	.	.	475
		St Dev	54	.	.	.	.	.	.	.	.	.	54
	4 C	Num	.	.	3	4	4	4	4	.	4	4	27
		Mean	.	.	614	448	465	548	449	.	374	380	463
		St Dev	.	.	26	22	20	15	4	.	75	12	83
	Room	Num	.	.	3	4	4	3	4	.	4	4	26
		Mean	.	.	561	411	460	475	355	.	263	269	390
		St Dev	.	.	63	47	5	29	25	.	42	11	106
Surface	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	395	.	.	.	.	.	.	.	.	.	395
		St Dev	10	.	.	.	.	.	.	.	.	.	10
	4 C	Num	.	4	.	3	4	4	4	4	.	4	27
		Mean	.	511	.	422	474	433	528	423	.	427	461
		St Dev	.	38	.	15	48	12	31	15	.	78	56
	Room	Num	.	4	.	4	4	3	4	4	.	3	26
		Mean	.	443	.	380	551	378	439	282	.	124	380
		St Dev	.	51	.	64	27	35	56	62	.	31	131

Stability of 1,1-Dichloroethylene in Environmental Water Samples



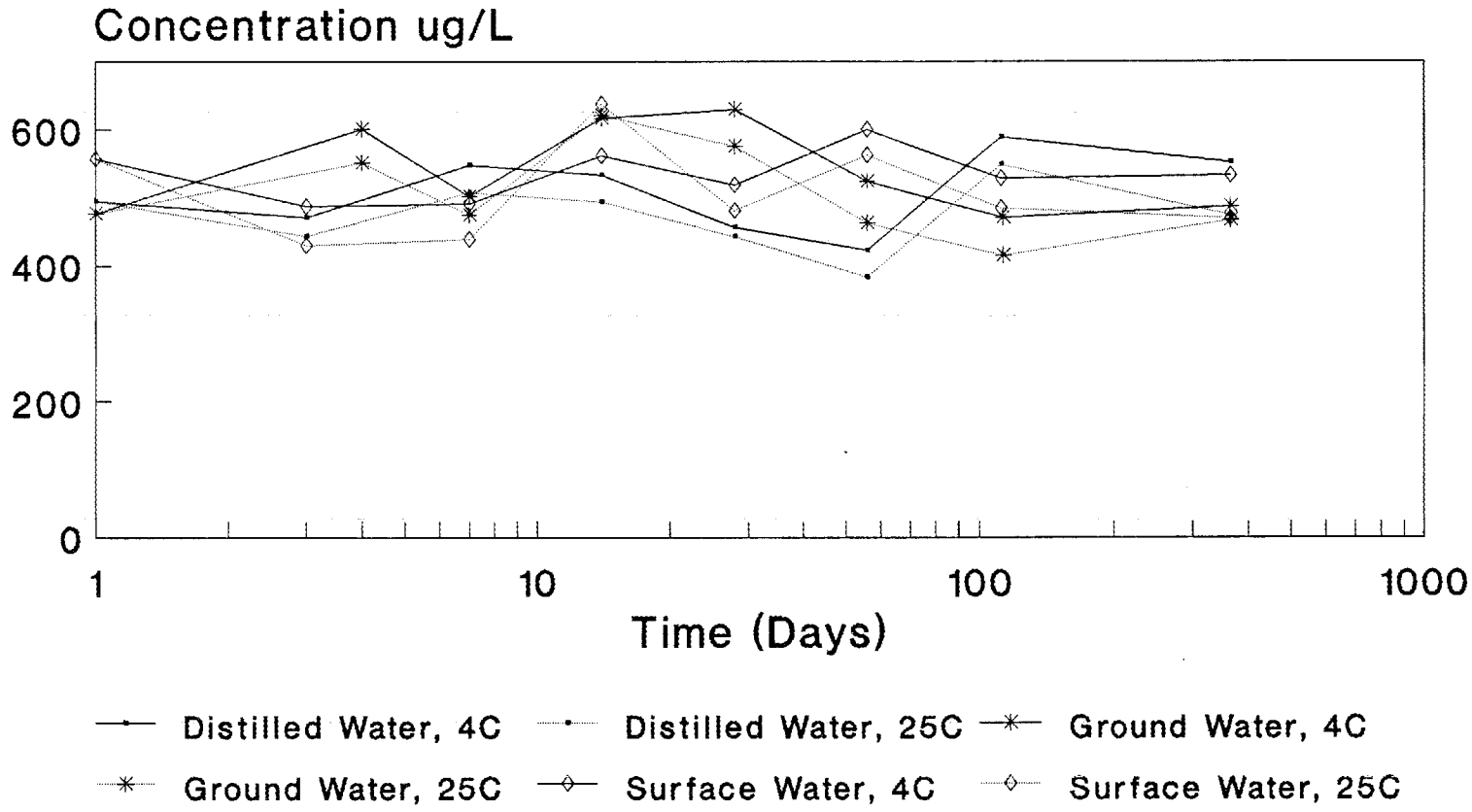
Initial Spike: 500 ug/L

Figure A.2

Table A.3 Summary Statistics for high level concentrations (μg/L) for 1,1-Dichloroethane.

Water	Storage Conditions		Days 0	3	4	7	14	28	56	112	113	365	All
Distilled	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	495	.	.	.	.	.	.	.	.	.	495
		St Dev	18	.	.	.	.	.	.	.	.	.	18
	4 C	Num	.	4	.	4	4	3	4	4	.	4	27
		Mean	.	471	.	548	534	457	423	589	.	553	513
		St Dev	.	3	.	36	9	13	24	10	.	13	59
	Room	Num	.	4	.	4	4	4	4	4	.	4	28
		Mean	.	444	.	508	494	443	383	549	.	475	471
		St Dev	.	38	.	42	56	29	25	46	.	35	62
Ground	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	477	.	.	.	.	.	.	.	.	.	477
		St Dev	37	.	.	.	.	.	.	.	.	.	37
	4 C	Num	.	.	3	4	4	4	4	.	4	4	27
		Mean	.	.	601	502	617	630	524	.	471	488	546
		St Dev	.	.	28	24	14	14	19	.	58	14	68
	Room	Num	.	.	3	4	4	3	4	.	4	4	26
		Mean	.	.	552	475	621	576	463	.	415	468	506
		St Dev	.	.	63	46	13	45	37	.	63	22	80
Surface	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	557	.	.	.	.	.	.	.	.	.	557
		St Dev	16	.	.	.	.	.	.	.	.	.	16
	4 C	Num	.	4	.	3	4	4	4	4	.	4	27
		Mean	.	488	.	491	562	519	600	529	.	534	533
		St Dev	.	38	.	33	36	19	21	5	.	77	51
	Room	Num	.	4	.	4	4	3	4	4	.	3	26
		Mean	.	430	.	439	638	481	563	485	.	470	503
		St Dev	.	41	.	77	23	50	54	32	.	12	83

Stability of 1,1-Dichloroethane in Environmental Water Samples



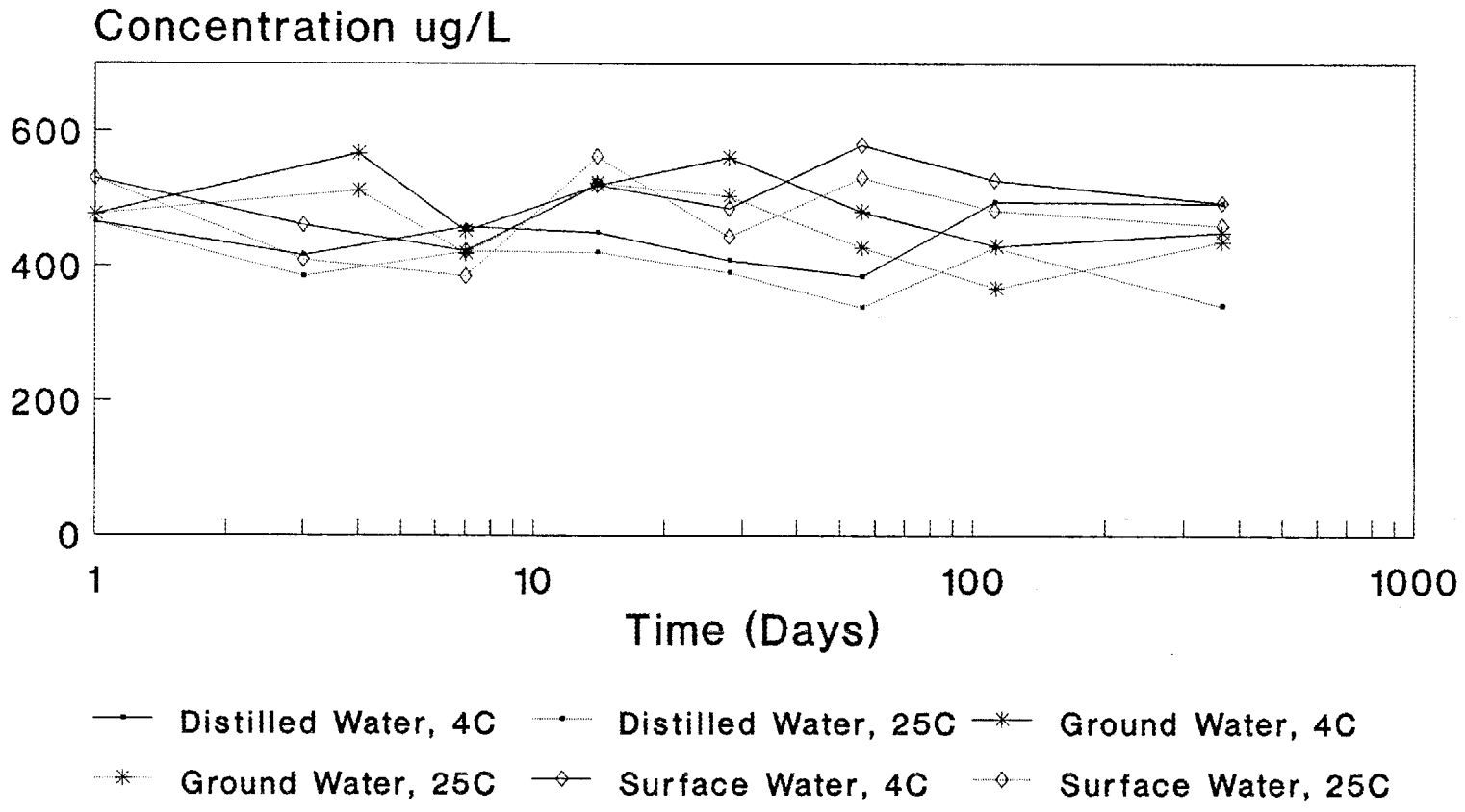
Initial Spike: 500 ug/L

Figure A.3

Table A.4 Summary Statistics for high level concentrations (μg/L) for Chloroform.

Water	Storage Conditions		Days 0	3	4	7	14	28	56	112	113	365	All
Distilled	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	465	.	.	.	.	.	.	.	.	.	465
		St Dev	24	.	.	.	.	.	.	.	.	.	24
	4 C	Num	.	4	.	4	4	3	4	4	.	4	27
		Mean	.	416	.	458	450	409	385	496	.	493	445
		St Dev	.	7	.	30	16	14	22	13	.	18	43
	Room	Num	.	4	.	4	4	4	4	4	.	4	28
		Mean	.	385	.	422	421	391	339	428	.	341	390
		St Dev	.	33	.	33	45	27	29	32	.	27	46
Ground	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	477	.	.	.	.	.	.	.	.	.	477
		St Dev	43	.	.	.	.	.	.	.	.	.	43
	4 C	Num	.	.	3	4	4	4	4	.	4	4	27
		Mean	.	.	567	452	520	561	481	.	430	450	492
		St Dev	.	.	5	24	21	18	12	.	63	22	58
	Room	Num	.	.	3	4	4	3	4	.	4	4	26
		Mean	.	.	512	419	523	504	428	.	368	436	452
		St Dev	.	.	17	40	10	41	24	.	55	32	63
Surface	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	530	.	.	.	.	.	.	.	.	.	530
		St Dev	14	.	.	.	.	.	.	.	.	.	14
	4 C	Num	.	4	.	3	4	4	4	4	.	4	27
		Mean	.	461	.	423	521	486	580	528	.	494	502
		St Dev	.	36	.	33	27	13	30	2	.	52	53
	Room	Num	.	4	.	4	4	3	4	4	.	3	26
		Mean	.	410	.	385	563	444	532	483	.	460	469
		St Dev	.	46	.	77	8	49	55	32	.	21	74

Stability of Chloroform in Environmental Water Samples



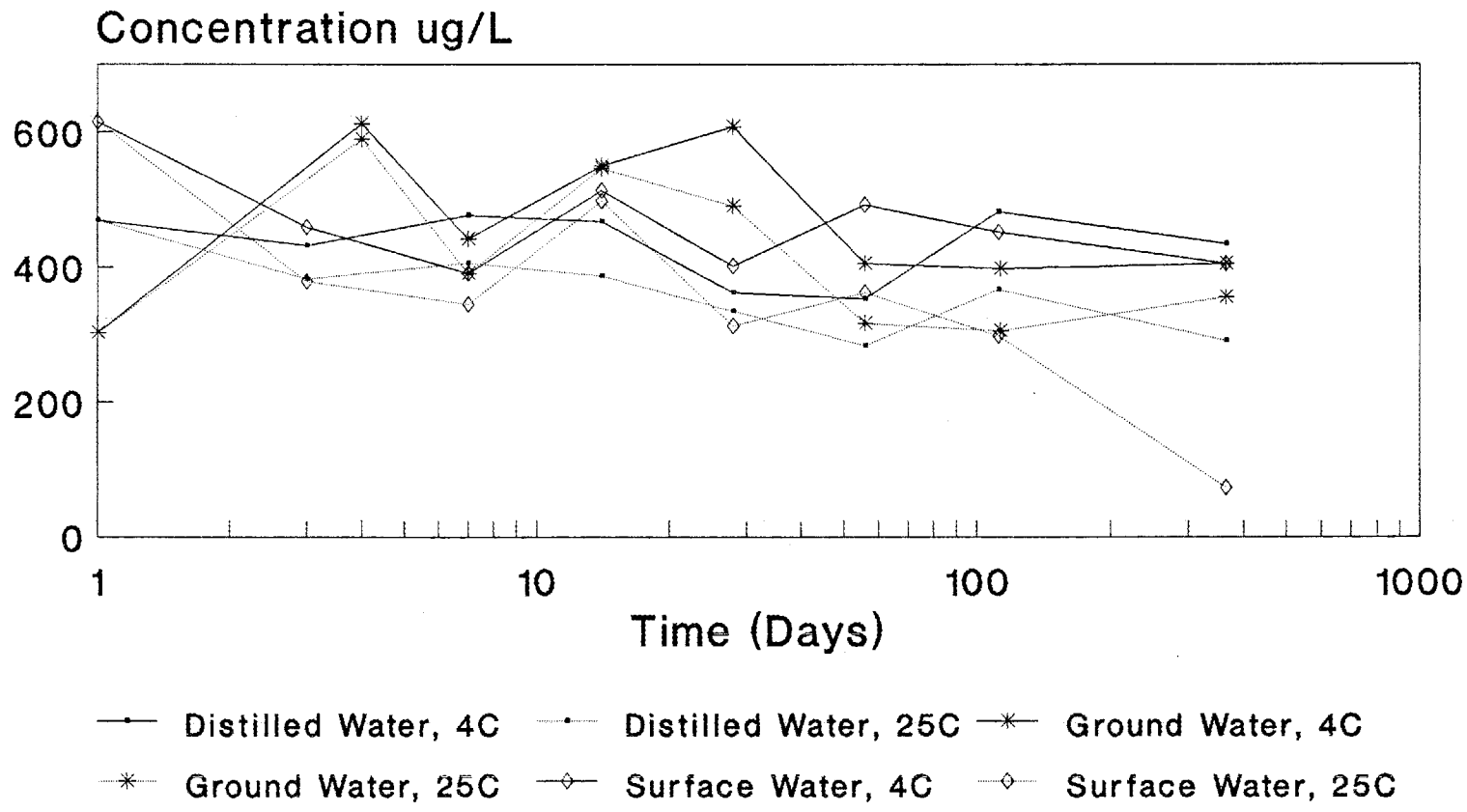
Initial Spike: 500 ug/L

Figure A.4

Table A.5 Summary Statistics for high level concentrations (μg/L) for Carbon Tetrachloride.

Water	Storage Conditions		Days 0	3	4	7	14	28	56	112	113	365	All
Distilled	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	469	.	.	.	.	.	.	.	.	.	469
		St Dev	29	.	.	.	.	.	.	.	.	.	29
	4 C	Num	.	4	.	4	4	3	4	4	.	4	27
		Mean	.	432	.	477	468	362	353	482	.	435	432
		St Dev	.	6	.	42	13	19	18	28	.	19	53
	Room	Num	.	4	.	4	4	4	4	4	.	4	28
		Mean	.	382	.	406	387	335	284	367	.	291	350
		St Dev	.	44	.	46	55	32	42	54	.	36	60
Ground	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	303	.	.	.	.	.	.	.	.	.	303
		St Dev	46	.	.	.	.	.	.	.	.	.	46
	4 C	Num	.	.	3	4	4	4	4	.	4	4	27
		Mean	.	.	612	442	550	608	405	.	398	405	484
		St Dev	.	.	22	33	20	16	19	.	76	17	96
	Room	Num	.	.	3	4	4	3	4	.	4	4	26
		Mean	.	.	589	391	546	490	316	.	305	356	419
		St Dev	.	.	69	61	14	60	38	.	53	22	113
Surface	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	615	.	.	.	.	.	.	.	.	.	615
		St Dev	19	.	.	.	.	.	.	.	.	.	19
	4 C	Num	.	4	.	3	4	4	4	4	.	4	27
		Mean	.	459	.	391	513	402	492	452	.	405	447
		St Dev	.	50	.	72	22	20	18	4	.	52	56
	Room	Num	.	4	.	4	4	3	4	4	.	3	26
		Mean	.	379	.	345	498	313	362	298	.	73	334
		St Dev	.	70	.	79	4	35	60	19	.	70	125

Stability of Carbon Tetrachloride in Environmental Water Samples



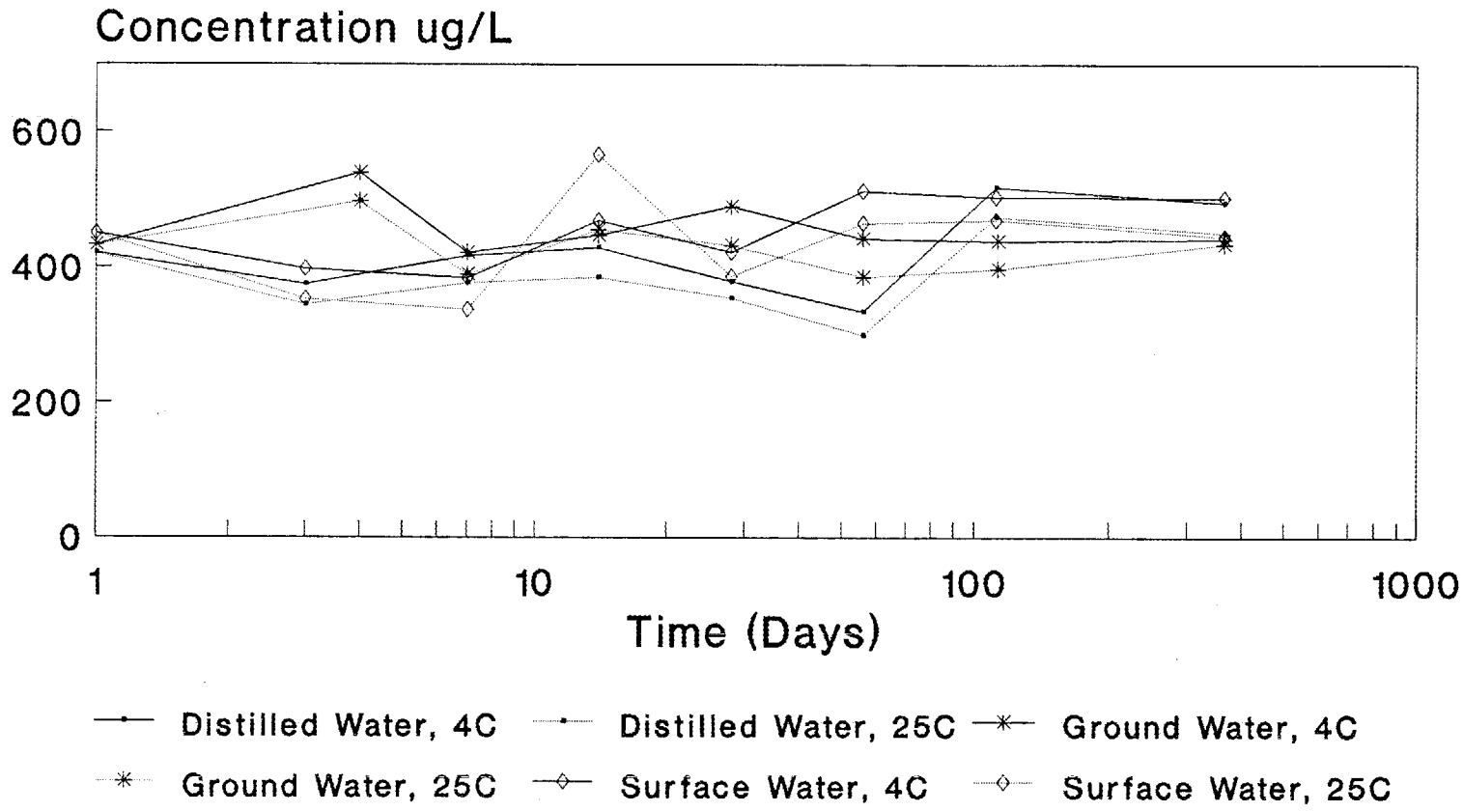
Initial Spike: 500 ug/L

Figure A.5

Table A.6 Summary Statistics for high level concentrations (μg/L) for 1,2-Dichloropropane.

Water	Storage Conditions		Days 0	3	4	7	14	28	56	112	113	365	All
Distilled	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	421	.	.	.	.	.	.	.	.	.	421
		St Dev	20	.	.	.	.	.	.	.	.	.	20
	4 C	Num	.	4	.	4	4	3	4	4	.	4	27
		Mean	.	375	.	417	429	380	335	519	.	496	423
		St Dev	.	7	.	29	9	15	24	20	.	6	65
	Room	Num	.	4	.	4	4	4	4	4	.	4	28
		Mean	.	345	.	377	385	355	300	475	.	451	384
		St Dev	.	35	.	32	47	30	28	43	.	23	65
Ground	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	433	.	.	.	.	.	.	.	.	.	433
		St Dev	34	.	.	.	.	.	.	.	.	.	34
	4 C	Num	.	.	3	4	4	4	4	.	4	4	27
		Mean	.	.	540	422	447	490	443	.	439	442	458
		St Dev	.	.	21	15	18	15	5	.	47	23	42
	Room	Num	.	.	3	4	4	3	4	.	4	4	26
		Mean	.	.	498	390	456	433	386	.	398	435	425
		St Dev	.	.	33	43	6	39	27	.	53	15	48
Surface	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	450	.	.	.	.	.	.	.	.	.	450
		St Dev	13	.	.	.	.	.	.	.	.	.	13
	4 C	Num	.	4	.	3	4	4	4	4	.	4	27
		Mean	.	398	.	384	469	423	513	504	.	503	459
		St Dev	.	32	.	42	38	13	25	9	.	61	59
	Room	Num	.	4	.	4	4	3	4	4	.	3	26
		Mean	.	353	.	338	566	387	466	470	.	446	433
		St Dev	.	40	.	74	24	46	43	30	.	15	86

Stability of 1,2-Dichloropropane in Environmental Water Samples



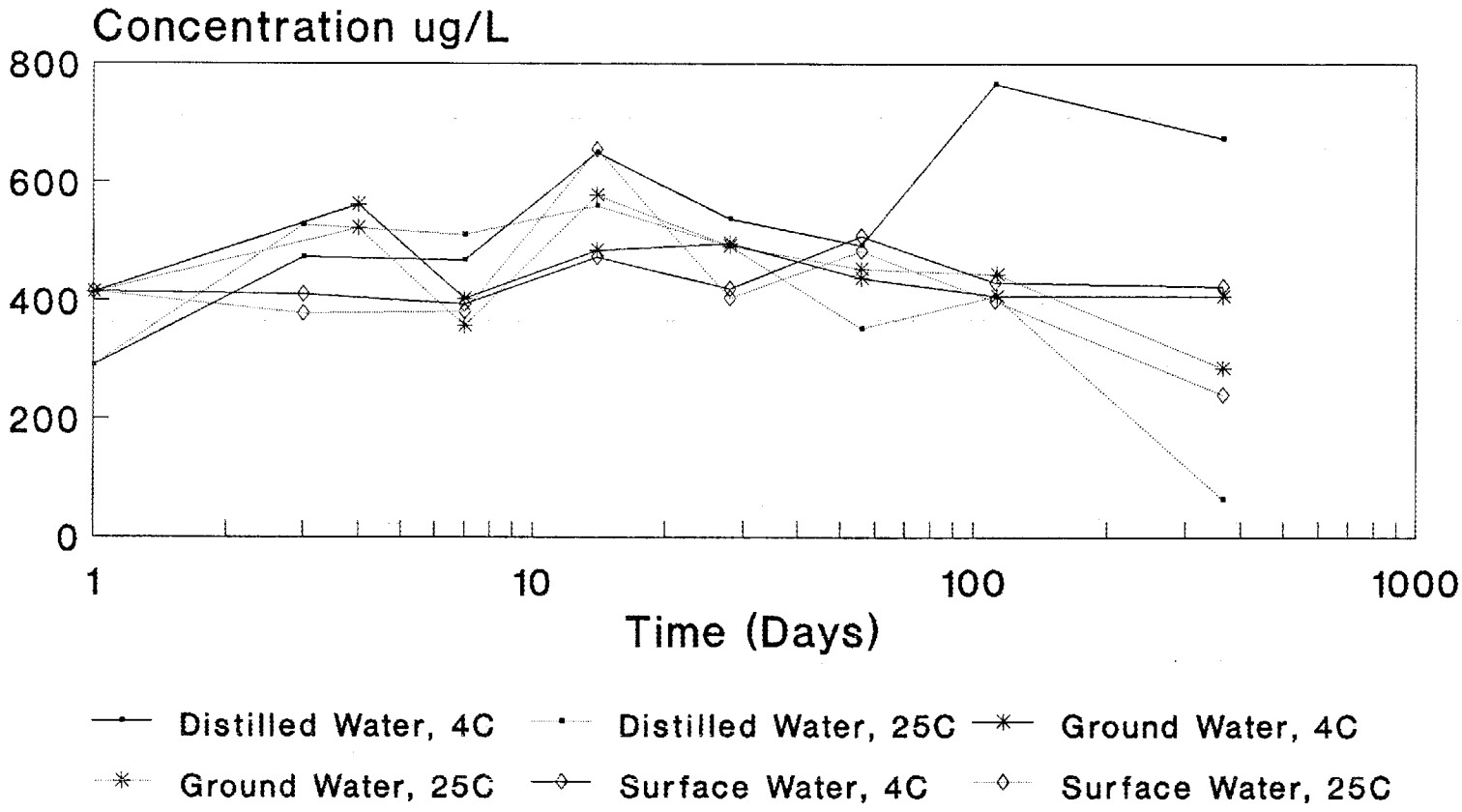
Initial Spike: 500 ug/L

Figure A.6

Table A.7 Summary Statistics for high level concentrations (μg/L) for Trichloroethylene.

Water	Storage Conditions		Days 0	3	4	7	14	28	56	112	113	365	All
Distilled	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	291	.	.	.	.	.	.	.	.	.	291
		St Dev	24	.	.	.	.	.	.	.	.	.	24
	4 C	Num	.	4	.	4	4	3	4	4	.	4	27
		Mean	.	474	.	468	650	539	494	766	.	675	583
		St Dev	.	66	.	43	37	32	53	55	.	83	122
	Room	Num	.	4	.	4	4	4	4	4	.	4	28
		Mean	.	528	.	511	560	493	353	408	.	64	417
		St Dev	.	54	.	43	73	45	57	104	.	51	171
Ground	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	414	.	.	.	.	.	.	.	.	.	414
		St Dev	29	.	.	.	.	.	.	.	.	.	29
	4 C	Num	.	.	3	4	4	4	4	.	4	4	27
		Mean	.	.	563	404	485	497	438	.	408	408	454
		St Dev	.	.	43	21	22	47	31	.	68	8	64
	Room	Num	.	.	3	4	4	3	4	.	4	4	26
		Mean	.	.	523	358	578	493	454	.	444	286	444
		St Dev	.	.	78	54	14	40	51	.	75	21	105
Surface	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	415	.	.	.	.	.	.	.	.	.	415
		St Dev	14	.	.	.	.	.	.	.	.	.	14
	4 C	Num	.	4	.	3	4	4	4	4	.	4	27
		Mean	.	411	.	394	474	420	509	431	.	424	439
		St Dev	.	28	.	13	46	24	40	12	.	45	47
	Room	Num	.	4	.	4	4	3	4	4	.	3	26
		Mean	.	378	.	382	656	405	484	399	.	241	428
		St Dev	.	61	.	99	27	48	90	94	.	34	134

Stability of Trichloroethylene in Environmental Water Samples



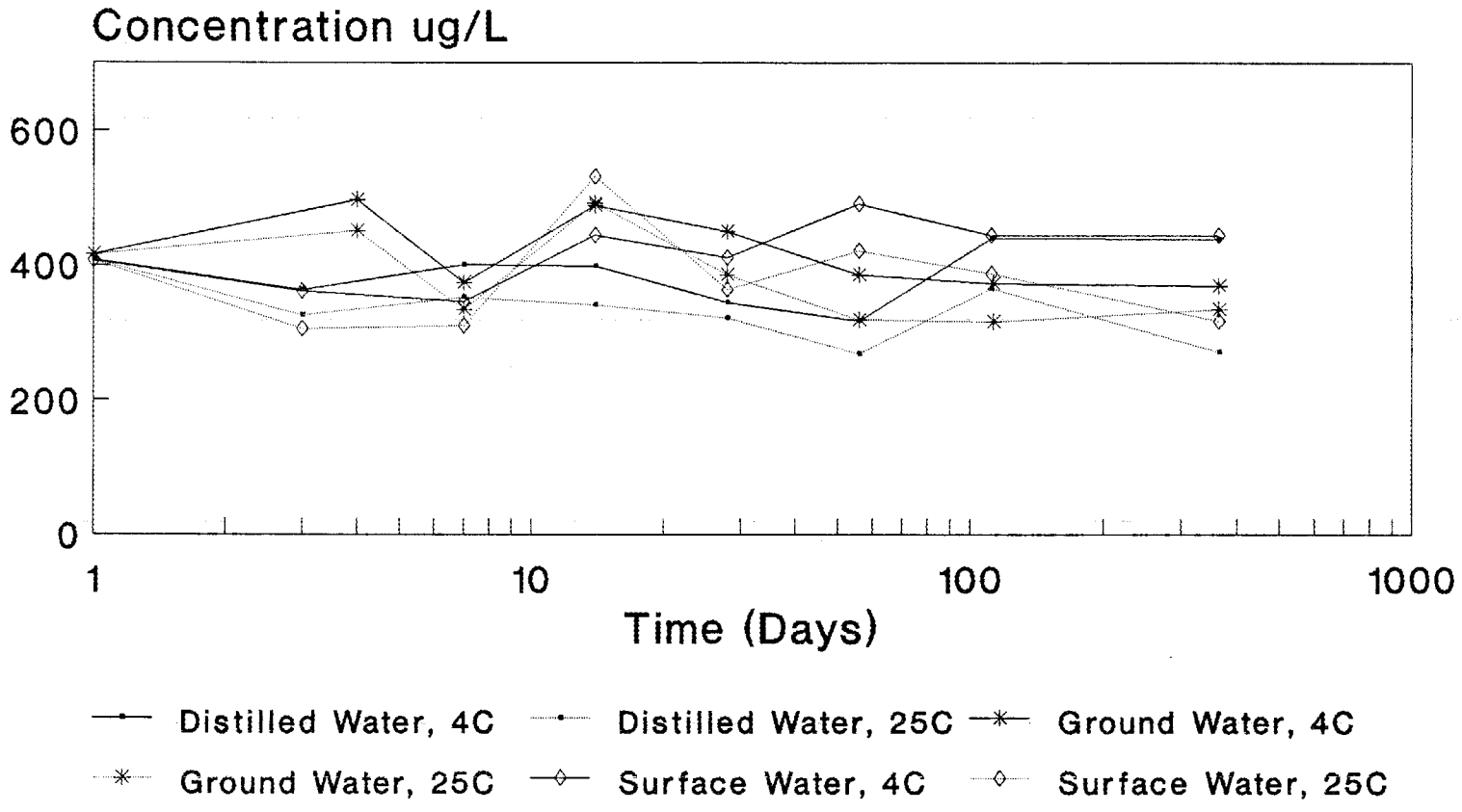
Initial Spike: 500 ug/L

Figure A.7

Table A.8 Summary Statistics for high level concentrations (μg/L) for Benzene.

Water	Storage Conditions		Days 0	3	4	7	14	28	56	112	113	365	All
Distilled	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	408	.	.	.	.	.	.	.	.	.	408
		St Dev	27	.	.	.	.	.	.	.	.	.	27
	4 C	Num	.	4	.	4	4	3	4	4	.	4	27
		Mean	.	363	.	401	399	345	317	440	.	439	388
		St Dev	.	9	.	33	15	15	24	16	.	11	47
	Room	Num	.	4	.	4	4	4	4	4	.	4	28
		Mean	.	326	.	352	341	322	269	366	.	272	321
		St Dev	.	34	.	33	46	27	30	42	.	47	49
Ground	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	416	.	.	.	.	.	.	.	.	.	416
		St Dev	50	.	.	.	.	.	.	.	.	.	50
	4 C	Num	.	.	3	4	4	4	4	.	4	4	27
		Mean	.	.	497	374	489	450	386	.	373	370	417
		St Dev	.	.	16	24	23	18	4	.	48	5	57
	Room	Num	.	.	3	4	4	3	4	.	4	4	26
		Mean	.	.	451	334	492	386	319	.	316	335	373
		St Dev	.	.	42	44	5	34	24	.	50	14	73
Surface	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	407	.	.	.	.	.	.	.	.	.	407
		St Dev	12	.	.	.	.	.	.	.	.	.	12
	4 C	Num	.	4	.	3	4	4	4	4	.	4	27
		Mean	.	361	.	346	445	412	491	445	.	445	424
		St Dev	.	43	.	37	42	9	18	7	.	57	56
	Room	Num	.	4	.	4	4	3	4	4	.	3	26
		Mean	.	305	.	310	532	364	422	388	.	317	380
		St Dev	.	42	.	76	24	42	54	37	.	28	89

Stability of Benzene in Environmental Water Samples



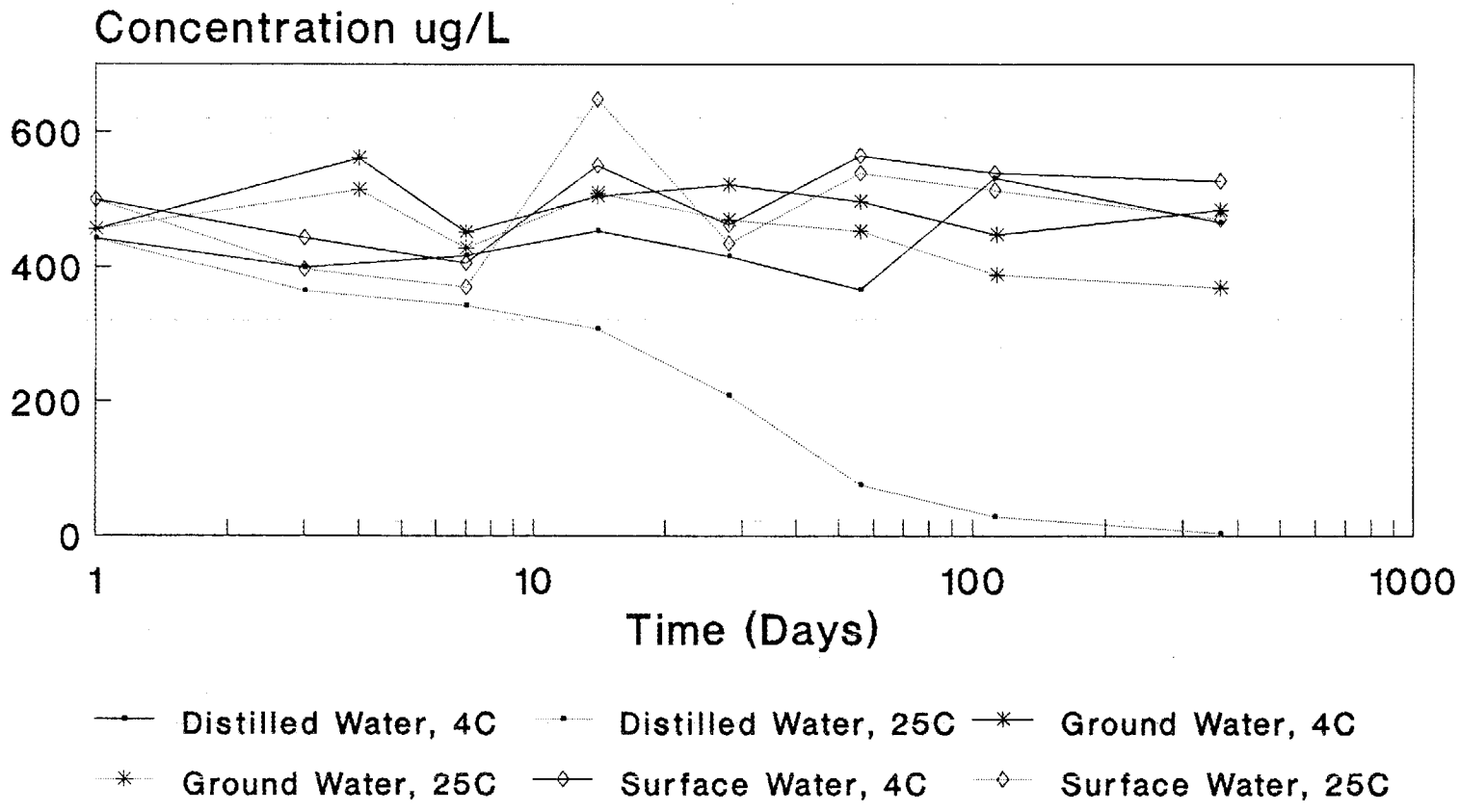
Initial Spike: 500 ug/L

Figure A.8

Table A.9 Summary Statistics for high level concentrations (μg/L) for 1,1,2-Trichloroethane.

Water	Storage Conditions		Days 0	3	4	7	14	28	56	112	113	365	All
Distilled	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	442	.	.	.	.	.	.	.	.	.	442
		St Dev	17	.	.	.	.	.	.	.	.	.	17
	4 C	Num	.	4	.	4	4	3	4	4	.	4	27
		Mean	.	399	.	416	453	415	366	532	.	466	436
		St Dev	.	12	.	24	11	8	24	32	.	7	54
	Room	Num	.	4	.	4	4	4	4	4	.	4	28
		Mean	.	364	.	342	307	208	76	28	.	3	190
		St Dev	.	30	.	25	37	20	11	8	.	1	146
Ground	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	456	.	.	.	.	.	.	.	.	.	456
		St Dev	22	.	.	.	.	.	.	.	.	.	22
	4 C	Num	.	.	3	4	4	4	4	.	4	4	27
		Mean	.	.	561	451	504	522	497	.	447	484	493
		St Dev	.	.	13	19	14	15	6	.	53	8	42
	Room	Num	.	.	3	4	4	3	4	.	4	4	26
		Mean	.	.	514	427	509	469	453	.	388	369	443
		St Dev	.	.	32	40	12	40	33	.	52	15	61
Surface	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	500	.	.	.	.	.	.	.	.	.	500
		St Dev	7	.	.	.	.	.	.	.	.	.	7
	4 C	Num	.	4	.	3	4	4	4	4	.	4	27
		Mean	.	443	.	405	550	462	565	539	.	527	502
		St Dev	.	35	.	53	46	16	22	5	.	52	64
	Room	Num	.	4	.	4	4	3	4	4	.	3	26
		Mean	.	396	.	370	648	435	539	513	.	470	484
		St Dev	.	29	.	88	20	50	38	29	.	14	101

Stability of 1,1,2-Trichloroethane in Environmental Water Samples



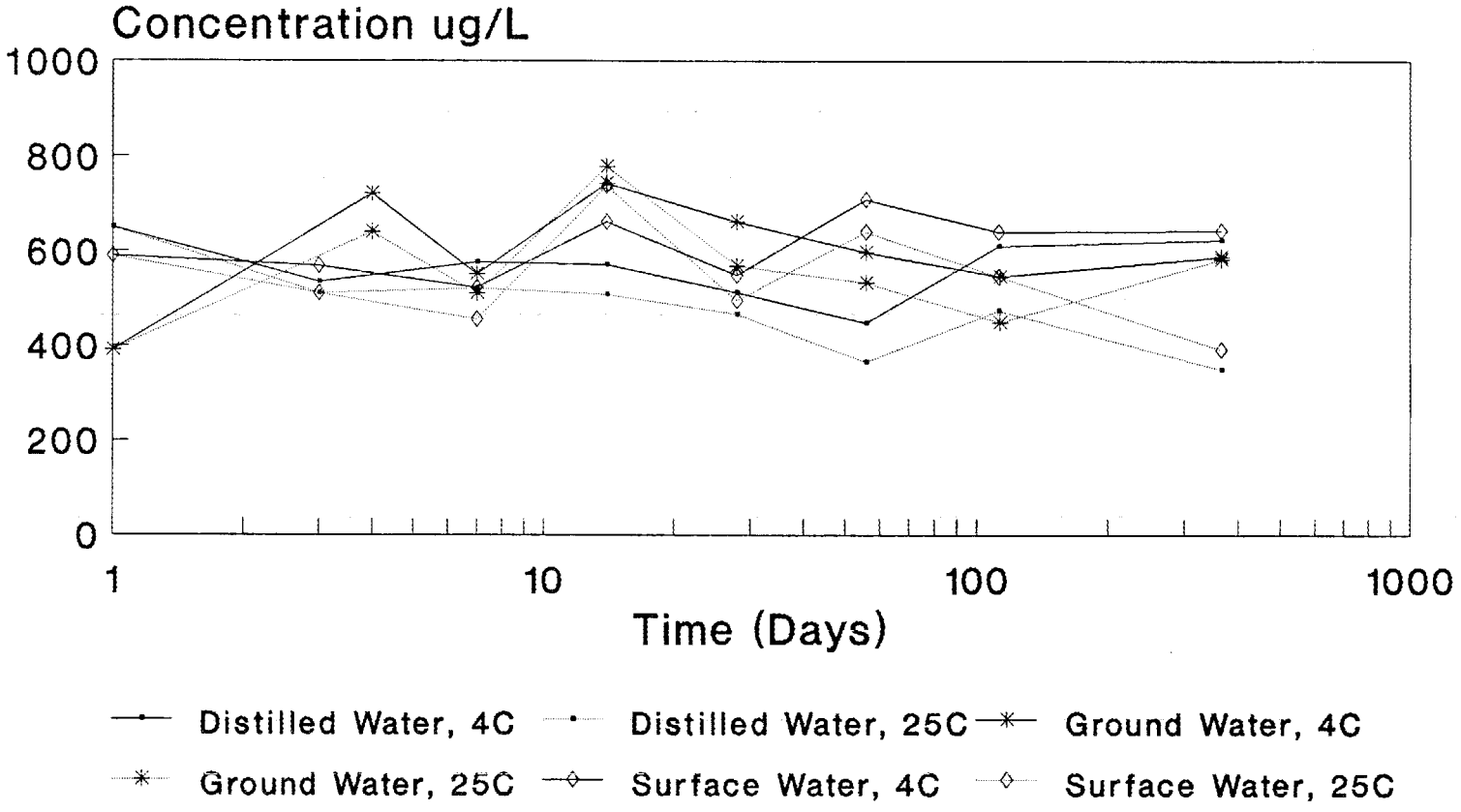
Initial Spike: 500 ug/L

Figure A.9

Table A.10 Summary Statistics for high level concentrations (μg/L) for Bromoform.

Water	Storage Conditions		Days 0	3	4	7	14	28	56	112	113	365	All
Distilled	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	649	.	.	.	.	.	.	.	.	.	649
		St Dev	30	.	.	.	.	.	.	.	.	.	30
	4 C	Num	.	4	.	4	4	3	4	4	.	4	27
		Mean	.	535	.	577	571	512	448	610	.	623	555
		St Dev	.	16	.	44	16	15	33	27	.	6	62
	Room	Num	.	4	.	4	4	4	4	4	.	4	28
		Mean	.	511	.	521	508	467	366	474	.	350	457
		St Dev	.	56	.	45	69	44	50	51	.	25	80
Ground	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	390	.	.	.	.	.	.	.	.	.	390
		St Dev	20	.	.	.	.	.	.	.	.	.	20
	4 C	Num	.	.	3	4	4	4	4	.	4	4	27
		Mean	.	.	721	552	742	661	597	.	546	588	626
		St Dev	.	.	21	24	16	29	22	.	81	25	81
	Room	Num	.	.	3	4	4	3	4	.	4	4	26
		Mean	.	.	640	511	778	568	533	.	450	583	579
		St Dev	.	.	63	60	32	59	53	.	64	8	112
Surface	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	589	.	.	.	.	.	.	.	.	.	589
		St Dev	12	.	.	.	.	.	.	.	.	.	12
	4 C	Num	.	4	.	3	4	4	4	4	.	4	27
		Mean	.	568	.	523	662	549	709	641	.	643	617
		St Dev	.	41	.	96	33	20	20	8	.	55	73
	Room	Num	.	4	.	4	4	3	4	4	.	3	26
		Mean	.	511	.	456	738	495	641	546	.	392	547
		St Dev	.	53	.	153	33	71	66	33	.	59	129

Stability of Bromoform in Environmental Water Samples



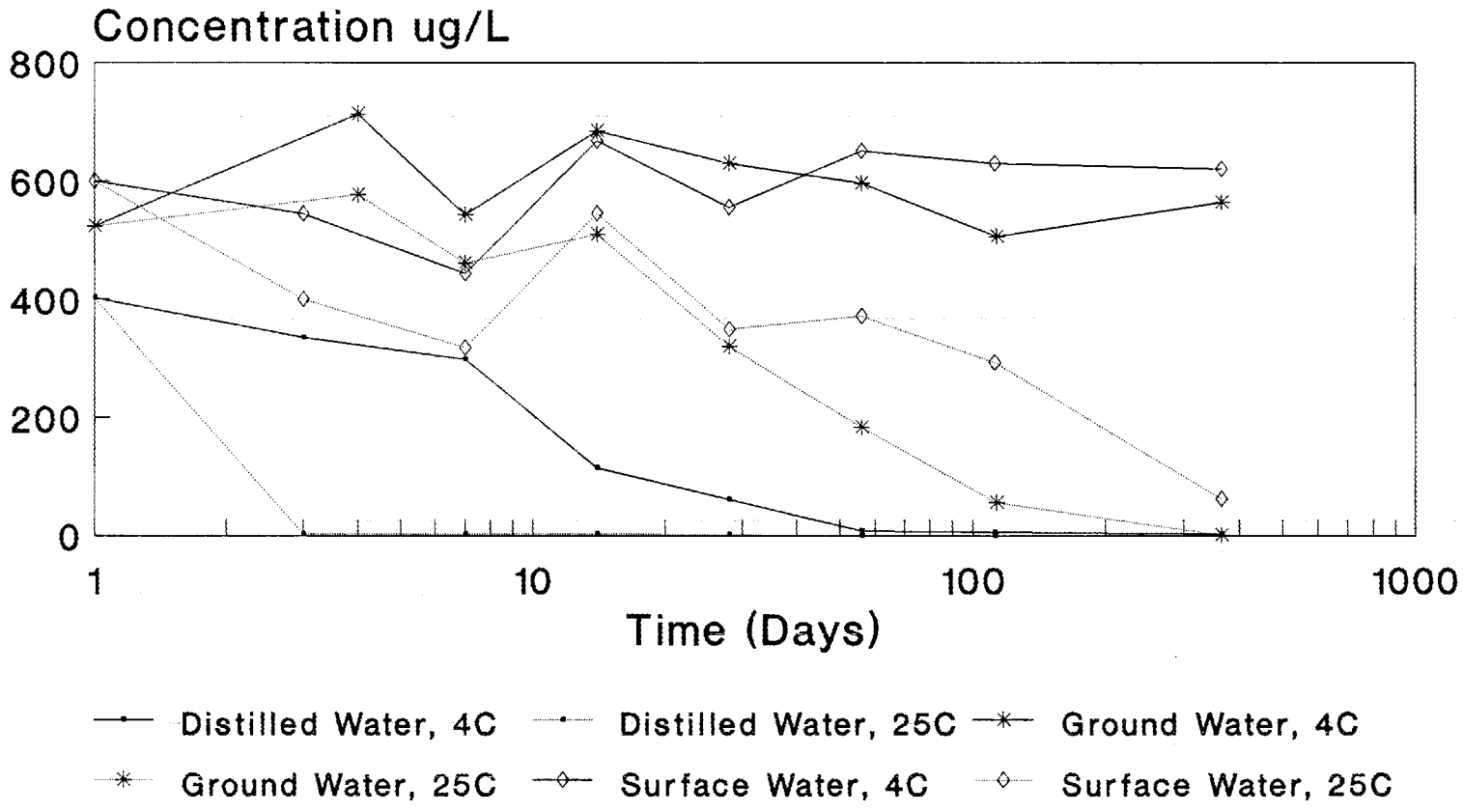
Initial Spike: 500 ug/L

Figure A.10

Table A.11 Summary Statistics for high level concentrations (μg/L) for 1,1,2,2-Tetrachloroethane.

Water	Storage Conditions		Days 0	3	4	7	14	28	56	112	113	365	All
Distilled	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	403	.	.	.	.	.	.	.	.	.	403
		St Dev	26	.	.	.	.	.	.	.	.	.	26
	4 C	Num	.	4	.	4	4	3	4	4	.	4	27
		Mean	.	336	.	299	115	61	8	6	.	3	120
		St Dev	.	21	.	23	13	34	1	1	.	1	137
	Room	Num	.	4	.	4	4	4	4	4	.	4	28
		Mean	.	3	.	3	3	2	0	0	.	1	2
		St Dev	.	1	.	1	0	1	1	0	.	1	1
Ground	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	524	.	.	.	.	.	.	.	.	.	524
		St Dev	7	.	.	.	.	.	.	.	.	.	7
	4 C	Num	.	.	3	4	4	4	4	.	4	4	27
		Mean	.	.	713	544	685	631	597	.	507	565	602
		St Dev	.	.	33	65	18	33	18	.	57	20	77
	Room	Num	.	.	3	4	4	3	4	.	4	4	26
		Mean	.	.	577	462	510	321	184	.	56	1	290
		St Dev	.	.	15	46	10	22	16	.	7	0	216
Surface	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	600	.	.	.	.	.	.	.	.	.	600
		St Dev	16	.	.	.	.	.	.	.	.	.	16
	4 C	Num	.	4	.	3	4	4	4	4	.	4	27
		Mean	.	545	.	444	668	556	652	631	.	621	593
		St Dev	.	86	.	136	43	6	61	9	.	66	91
	Room	Num	.	4	.	4	4	3	4	4	.	3	26
		Mean	.	400	.	319	546	350	372	294	.	62	345
		St Dev	.	65	.	87	16	48	41	21	.	41	139

Stability of 1,1,2,2-Tetrachloroethane in Environmental Water Samples



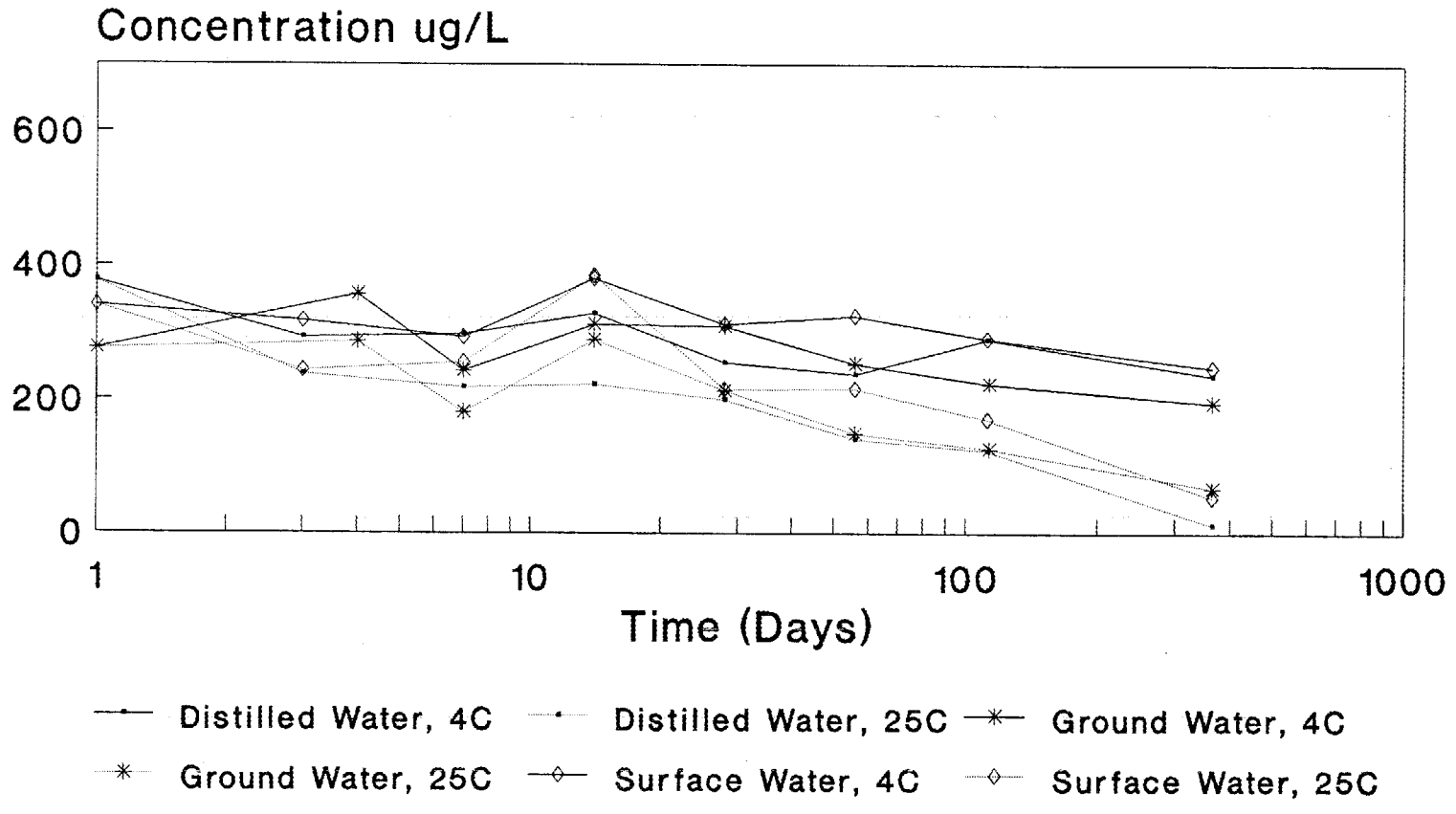
Initial Spike: 500 ug/L

Figure A.11

Table A.12 Summary Statistics for high level concentrations (μg/L) for Tetrachloroethylene.

Water	Storage Conditions		Days 0	3	4	7	14	28	56	112	113	365	All
Distilled	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	377	.	.	.	.	.	.	.	.	.	377
		St Dev	33	.	.	.	.	.	.	.	.	.	33
	4 C	Num	.	4	.	4	4	3	4	4	.	4	27
		Mean	.	293	.	297	328	255	238	290	.	236	277
		St Dev	.	11	.	37	23	25	32	32	.	34	41
	Room	Num	.	4	.	4	4	4	4	4	.	4	28
		Mean	.	238	.	218	222	199	141	123	.	12	165
		St Dev	.	30	.	23	29	21	34	40	.	12	79
Ground	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	275	.	.	.	.	.	.	.	.	.	275
		St Dev	17	.	.	.	.	.	.	.	.	.	17
	4 C	Num	.	.	3	4	4	4	4	.	4	4	27
		Mean	.	.	357	242	312	309	253	.	223	195	267
		St Dev	.	.	21	27	10	24	22	.	41	11	57
	Room	Num	.	.	3	4	4	3	4	.	4	4	26
		Mean	.	.	286	180	289	213	149	.	126	67	182
		St Dev	.	.	57	30	9	13	21	.	17	6	81
Surface	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	340	.	.	.	.	.	.	.	.	.	340
		St Dev	10	.	.	.	.	.	.	.	.	.	10
	4 C	Num	.	4	.	3	4	4	4	4	.	4	27
		Mean	.	317	.	293	381	312	325	291	.	248	310
		St Dev	.	55	.	35	35	10	14	19	.	41	49
	Room	Num	.	4	.	4	4	3	4	4	.	3	26
		Mean	.	243	.	255	385	215	216	170	.	54	226
		St Dev	.	52	.	73	18	27	48	52	.	18	100

Stability of Tetrachloroethylene in Environmental Water Samples



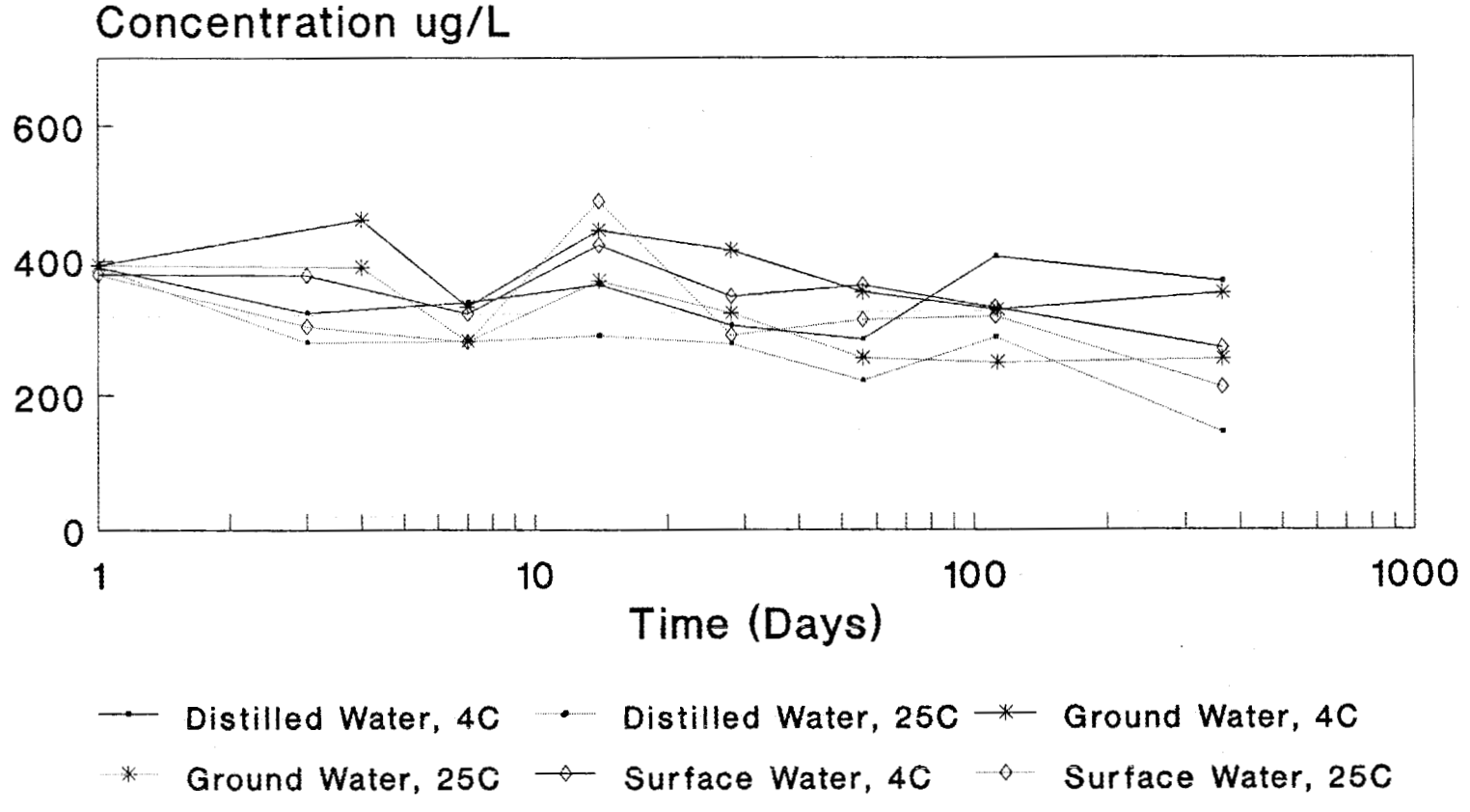
Initial Spike: 500 ug/L

Figure A.12

Table A.13 Summary Statistics for high level concentrations (μg/L) for Toluene.

Water	Storage Conditions		Days 0	3	4	7	14	28	56	112	113	365	All
Distilled	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	391	.	.	.	.	.	.	.	.	.	391
		St Dev	34	.	.	.	.	.	.	.	.	.	34
	4 C	Num	.	4	.	4	4	3	4	4	.	4	27
		Mean	.	322	.	338	364	304	283	405	.	369	342
		St Dev	.	15	.	36	18	22	34	27	.	17	46
	Room	Num	.	4	.	4	4	4	4	4	.	4	28
		Mean	.	278	.	280	288	276	221	285	.	144	253
		St Dev	.	30	.	21	42	28	39	45	.	43	60
Ground	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	393	.	.	.	.	.	.	.	.	.	393
		St Dev	23	.	.	.	.	.	.	.	.	.	23
	4 C	Num	.	.	3	4	4	4	4	.	4	4	27
		Mean	.	.	460	331	445	415	353	.	327	351	380
		St Dev	.	.	24	33	16	25	20	.	47	5	56
	Room	Num	.	.	3	4	4	3	4	.	4	4	26
		Mean	.	.	390	280	370	322	255	.	248	253	298
		St Dev	.	.	54	43	91	33	31	.	40	17	70
Surface	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	380	.	.	.	.	.	.	.	.	.	380
		St Dev	11	.	.	.	.	.	.	.	.	.	11
	4 C	Num	.	4	.	3	4	4	4	4	.	4	27
		Mean	.	378	.	321	423	347	363	329	.	270	348
		St Dev	.	57	.	50	43	18	17	14	.	33	56
	Room	Num	.	4	.	4	4	3	4	4	.	3	26
		Mean	.	302	.	279	488	289	312	316	.	211	319
		St Dev	.	53	.	86	15	38	53	44	.	31	92

Stability of Toluene in Environmental Water Samples



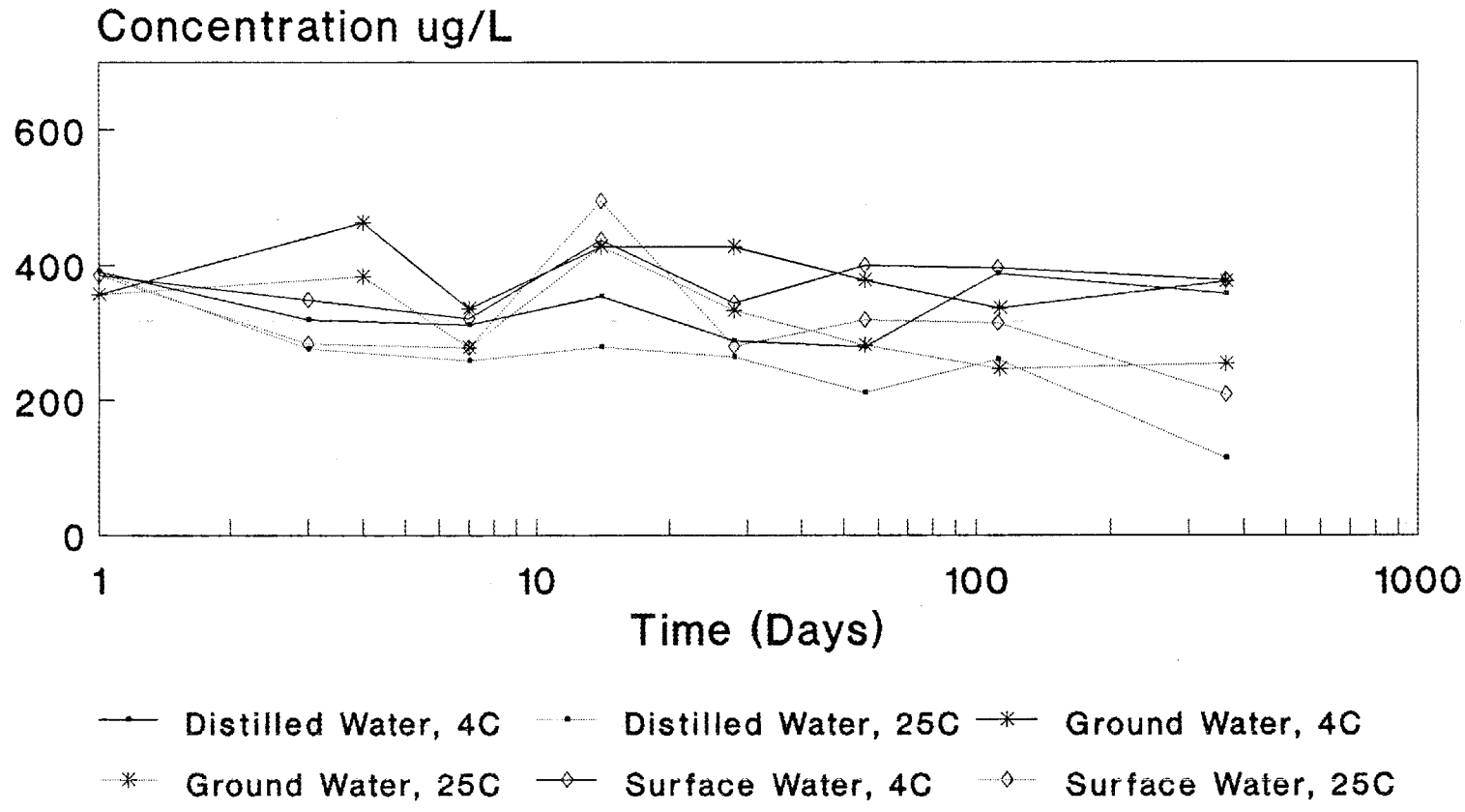
Initial Spike: 500 ug/L

Figure A.13

Table A.14 Summary Statistics for high level concentrations (μg/L) for Chlorobenzene.

Water	Storage Conditions		Days 0	3	4	7	14	28	56	112	113	365	All
Distilled	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	391	.	.	.	.	.	.	.	.	.	391
		St Dev	39	.	.	.	.	.	.	.	.	.	39
	4 C	Num	.	4	.	4	4	3	4	4	.	4	27
		Mean	.	319	.	312	354	288	279	388	.	358	330
		St Dev	.	15	.	36	25	25	36	35	.	22	45
	Room	Num	.	4	.	4	4	4	4	4	.	4	28
		Mean	.	276	.	259	279	264	211	261	.	114	238
		St Dev	.	28	.	19	40	26	43	42	.	41	64
Ground	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	357	.	.	.	.	.	.	.	.	.	357
		St Dev	24	.	.	.	.	.	.	.	.	.	24
	4 C	Num	.	.	3	4	4	4	4	.	4	4	27
		Mean	.	.	463	336	427	427	378	.	337	376	389
		St Dev	.	.	23	34	15	32	27	.	52	8	52
	Room	Num	.	.	3	4	4	3	4	.	4	4	26
		Mean	.	.	383	278	428	333	282	.	247	254	312
		St Dev	.	.	71	37	9	30	29	.	38	12	73
Surface	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	385	.	.	.	.	.	.	.	.	.	385
		St Dev	11	.	.	.	.	.	.	.	.	.	11
	4 C	Num	.	4	.	3	4	4	4	4	.	4	27
		Mean	.	349	.	321	437	344	400	396	.	378	377
		St Dev	.	56	.	58	32	20	16	3	.	39	48
	Room	Num	.	4	.	4	3	3	4	4	.	3	25
		Mean	.	284	.	278	495	280	319	315	.	208	309
		St Dev	.	43	.	100	22	39	46	46	.	28	91

Stability of Chlorobenzene in Environmental Water Samples



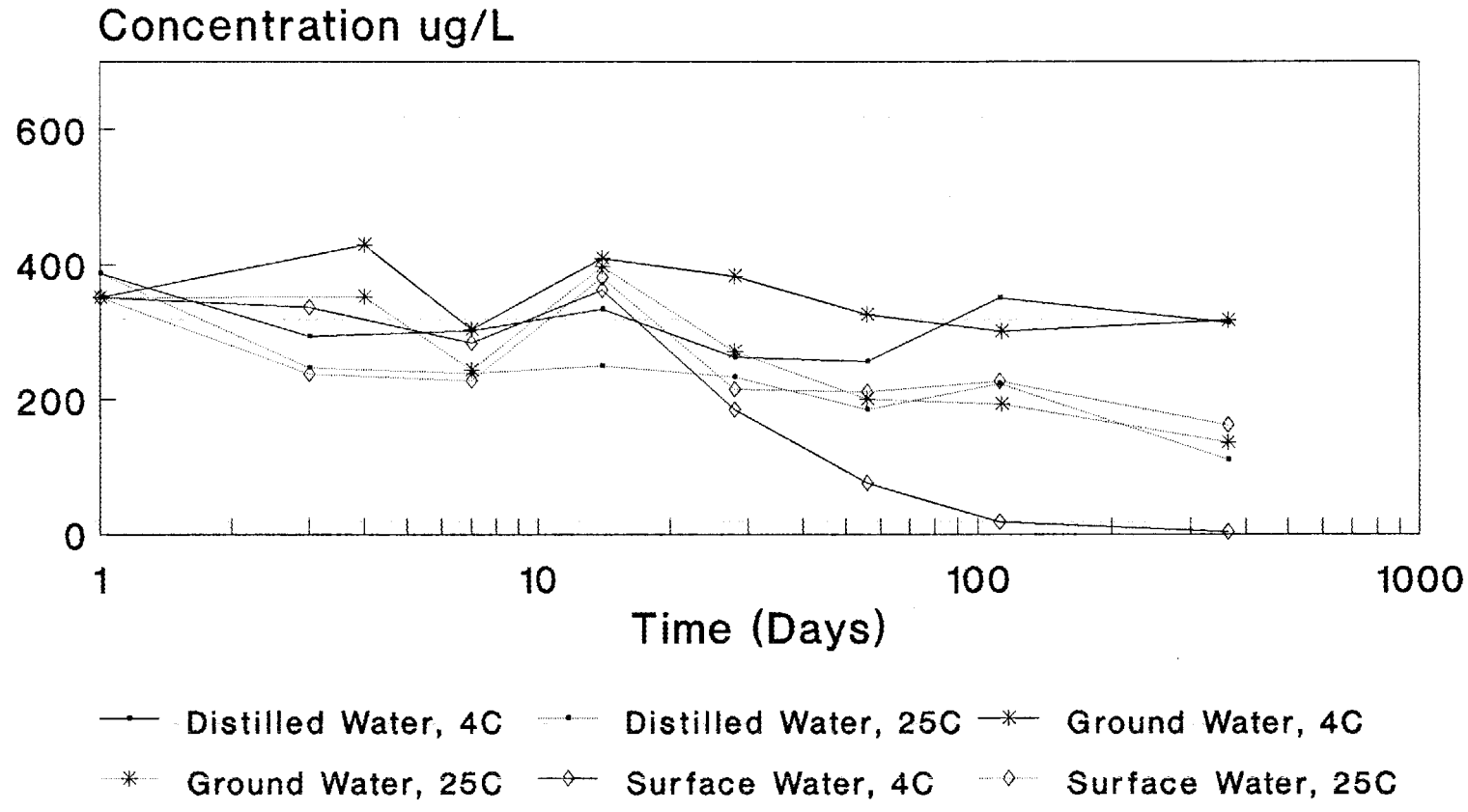
Initial Spike: 500 ug/L

Figure A.14

Table A.15 Summary Statistics for high level concentrations (μg/L) for Ethylbenzene.

Water	Storage Conditions		Days 0	3	4	7	14	28	56	112	113	365	All
Distilled	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	387	.	.	.	.	.	.	.	.	.	387
		St Dev	41	.	.	.	.	.	.	.	.	.	41
	4 C	Num	.	4	.	4	4	3	4	4	.	4	27
		Mean	.	294	.	302	334	262	256	350	.	314	303
		St Dev	.	15	.	37	25	27	36	34	.	21	41
	Room	Num	.	4	.	4	4	4	4	4	.	4	28
		Mean	.	247	.	239	250	233	185	223	.	110	212
		St Dev	.	27	.	19	37	23	43	38	.	35	56
Ground	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	351	.	.	.	.	.	.	.	.	.	351
		St Dev	25	.	.	.	.	.	.	.	.	.	25
	4 C	Num	.	.	3	4	4	4	4	.	4	4	27
		Mean	.	.	429	304	409	382	326	.	301	317	350
		St Dev	.	.	25	36	15	31	28	.	36	4	54
	Room	Num	.	.	3	4	4	3	4	.	4	4	26
		Mean	.	.	352	243	397	271	200	.	193	136	252
		St Dev	.	.	69	39	3	27	31	.	33	42	94
Surface	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	351	.	.	.	.	.	.	.	.	.	351
		St Dev	10	.	.	.	.	.	.	.	.	.	10
	4 C	Num	.	4	.	3	4	4	4	4	.	4	27
		Mean	.	337	.	284	362	185	76	18	.	3	177
		St Dev	.	64	.	46	35	11	23	7	.	2	147
	Room	Num	.	4	.	4	4	3	4	4	.	3	26
		Mean	.	238	.	228	381	215	211	227	.	162	241
		St Dev	.	49	.	85	5	24	39	46	.	23	76

Stability of Ethylbenzene in Environmental Water Samples



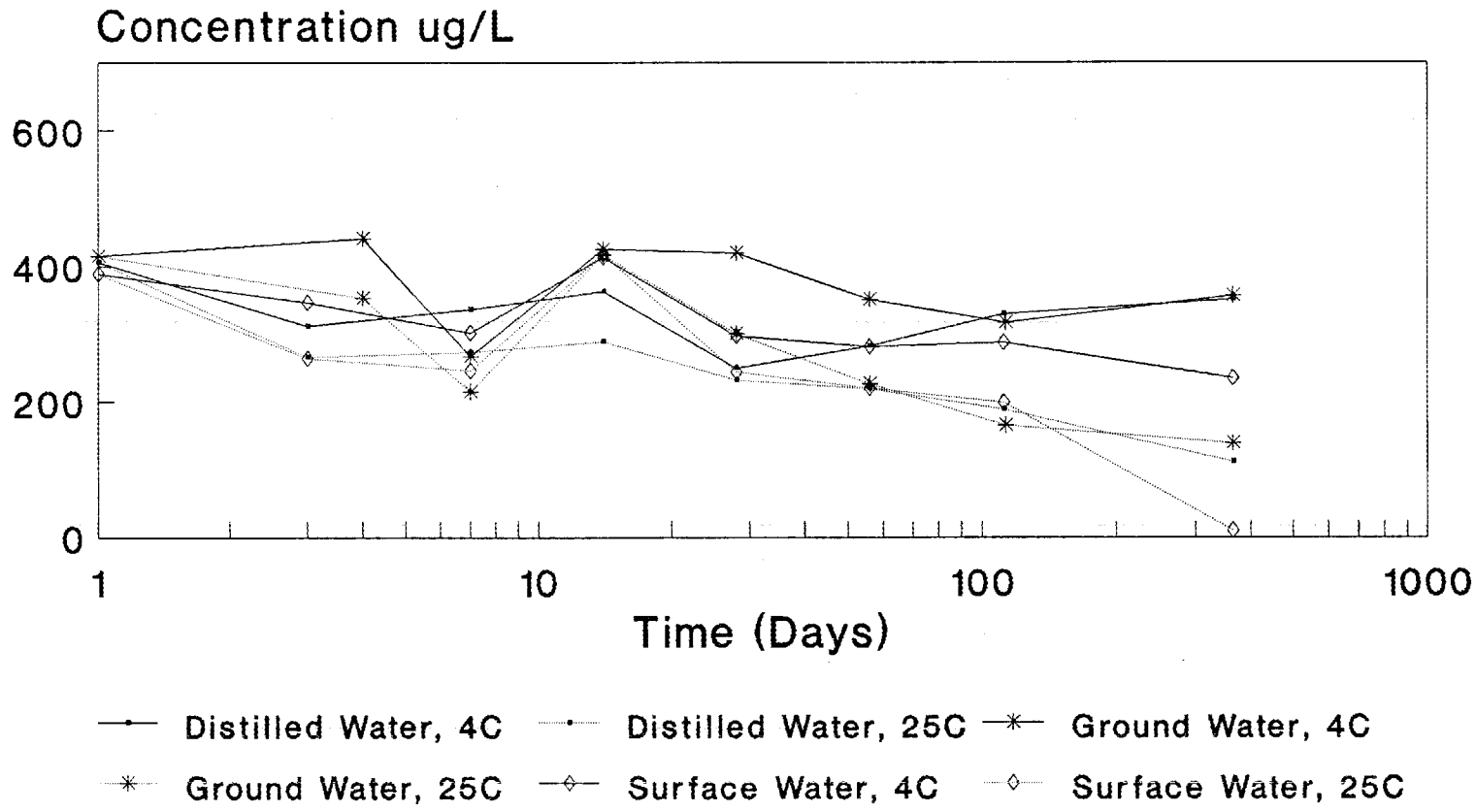
Initial Spike: 500 ug/L

Figure A.15

Table A.16 Summary Statistics for high level concentrations (μg/L) for Styrene.

Water	Storage Conditions		Days 0	3	4	7	14	28	56	112	113	365	All
Distilled	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	406	.	.	.	.	.	.	.	.	.	406
		St Dev	44	.	.	.	.	.	.	.	.	.	44
	4 C	Num	.	4	.	4	4	3	4	4	.	4	27
		Mean	.	312	.	337	363	250	283	330	.	351	321
		St Dev	.	17	.	40	24	22	39	20	.	23	43
	Room	Num	.	4	.	4	4	4	4	4	.	4	28
		Mean	.	266	.	273	289	232	219	189	.	111	226
		St Dev	.	28	.	22	43	19	45	56	.	39	67
Ground	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	415	.	.	.	.	.	.	.	.	.	415
		St Dev	32	.	.	.	.	.	.	.	.	.	32
	4 C	Num	.	.	3	4	4	4	4	.	4	4	27
		Mean	.	.	441	267	425	420	351	.	317	357	366
		St Dev	.	.	21	31	13	41	38	.	60	7	67
	Room	Num	.	.	3	4	4	3	3	.	3	3	23
		Mean	.	.	353	215	417	301	227	.	165	139	265
		St Dev	.	.	71	34	5	34	40	.	48	14	103
Surface	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	389	.	.	.	.	.	.	.	.	.	389
		St Dev	18	.	.	.	.	.	.	.	.	.	18
	4 C	Num	.	4	.	3	4	4	4	4	.	4	27
		Mean	.	347	.	302	414	297	282	288	.	235	310
		St Dev	.	60	.	59	31	26	12	17	.	39	64
	Room	Num	.	4	.	4	4	3	4	4	.	3	26
		Mean	.	264	.	246	418	244	220	199	.	10	237
		St Dev	.	47	.	98	7	30	53	71	.	17	120

Stability of Styrene in Environmental Water Samples



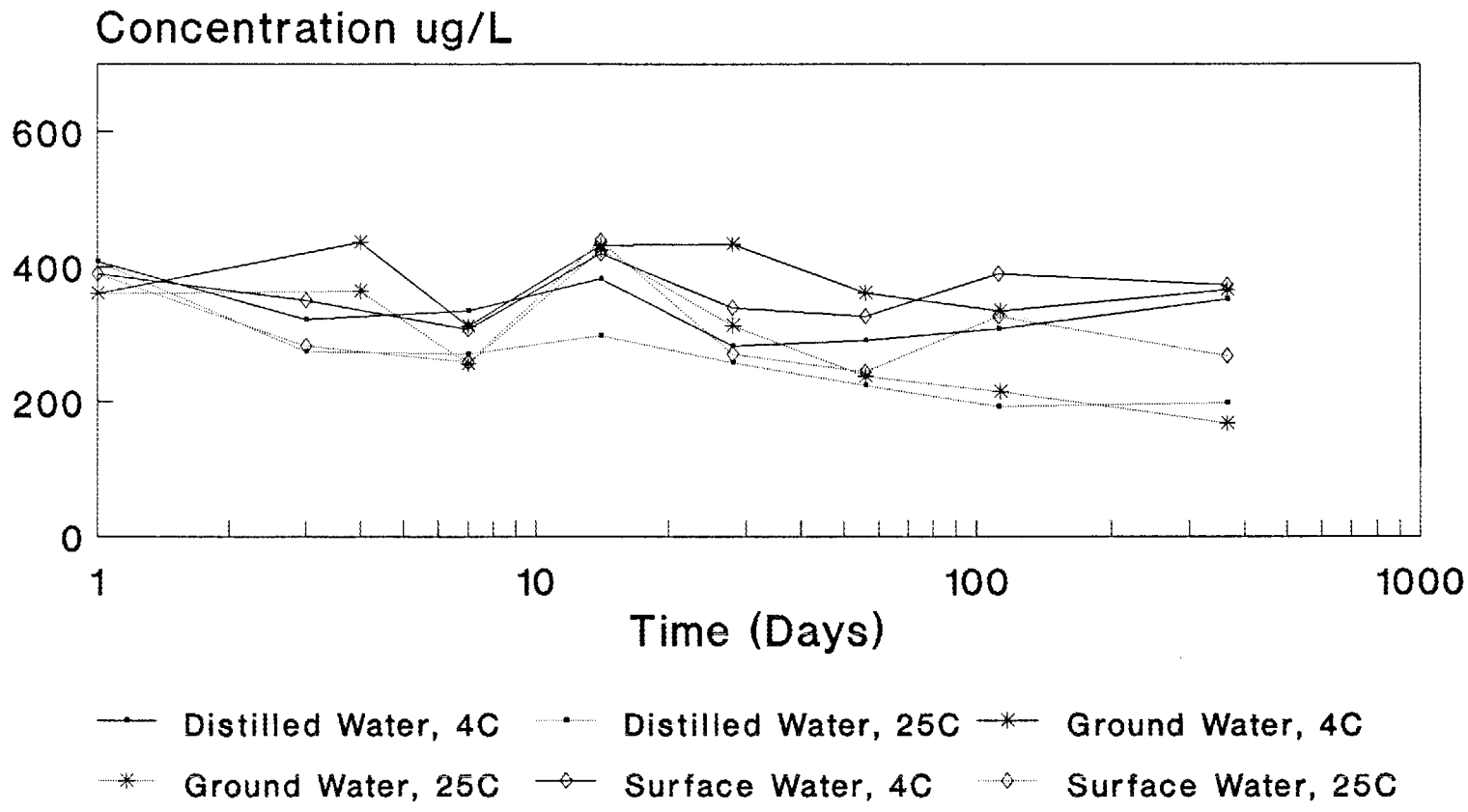
Initial Spike: 500 ug/L

Figure A.16

Table A.17 Summary Statistics for high level concentrations (μg/L) for <u>O-Xylene</u>.

Water	Storage Conditions		Days 0	3	4	7	14	28	56	112	113	365	All
Distilled	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	408	.	.	.	.	.	.	.	.	.	408
		St Dev	43	.	.	.	.	.	.	.	.	.	43
	4 C	Num	.	4	.	4	4	3	4	4	.	4	27
		Mean	.	322	.	335	382	283	291	308	.	352	326
		St Dev	.	16	.	41	27	26	35	37	.	15	42
	Room	Num	.	4	.	4	4	4	4	4	.	4	28
		Mean	.	274	.	271	298	258	224	193	.	198	245
		St Dev	.	28	.	22	45	24	46	29	.	34	48
Ground	None	Num	3	.	.	.	.	.	.	.	.	.	3
		Mean	360	.	.	.	.	.	.	.	.	.	360
		St Dev	24	.	.	.	.	.	.	.	.	.	24
	4 C	Num	.	.	3	4	4	4	4	.	4	4	27
		Mean	.	.	436	312	432	434	361	.	335	366	380
		St Dev	.	.	27	34	15	35	34	.	36	9	55
	Room	Num	.	.	3	4	4	3	4	.	4	3	25
		Mean	.	.	364	256	425	313	238	.	215	168	283
		St Dev	.	.	75	36	5	27	36	.	44	35	92
Surface	None	Num	4	.	.	.	.	.	.	.	.	.	4
		Mean	390	.	.	.	.	.	.	.	.	.	390
		St Dev	13	.	.	.	.	.	.	.	.	.	13
	4 C	Num	.	4	.	3	4	4	4	4	.	4	27
		Mean	.	350	.	307	420	339	327	390	.	373	360
		St Dev	.	59	.	63	27	23	15	9	.	33	48
	Room	Num	.	4	.	4	4	3	4	4	.	3	26
		Mean	.	283	.	259	438	271	244	327	.	268	301
		St Dev	.	45	.	77	3	38	49	31	.	20	76

Stability of o-Xylene in Environmental Water Samples



Initial Spike: 500 ug/L

Figure A.17

Appendix B

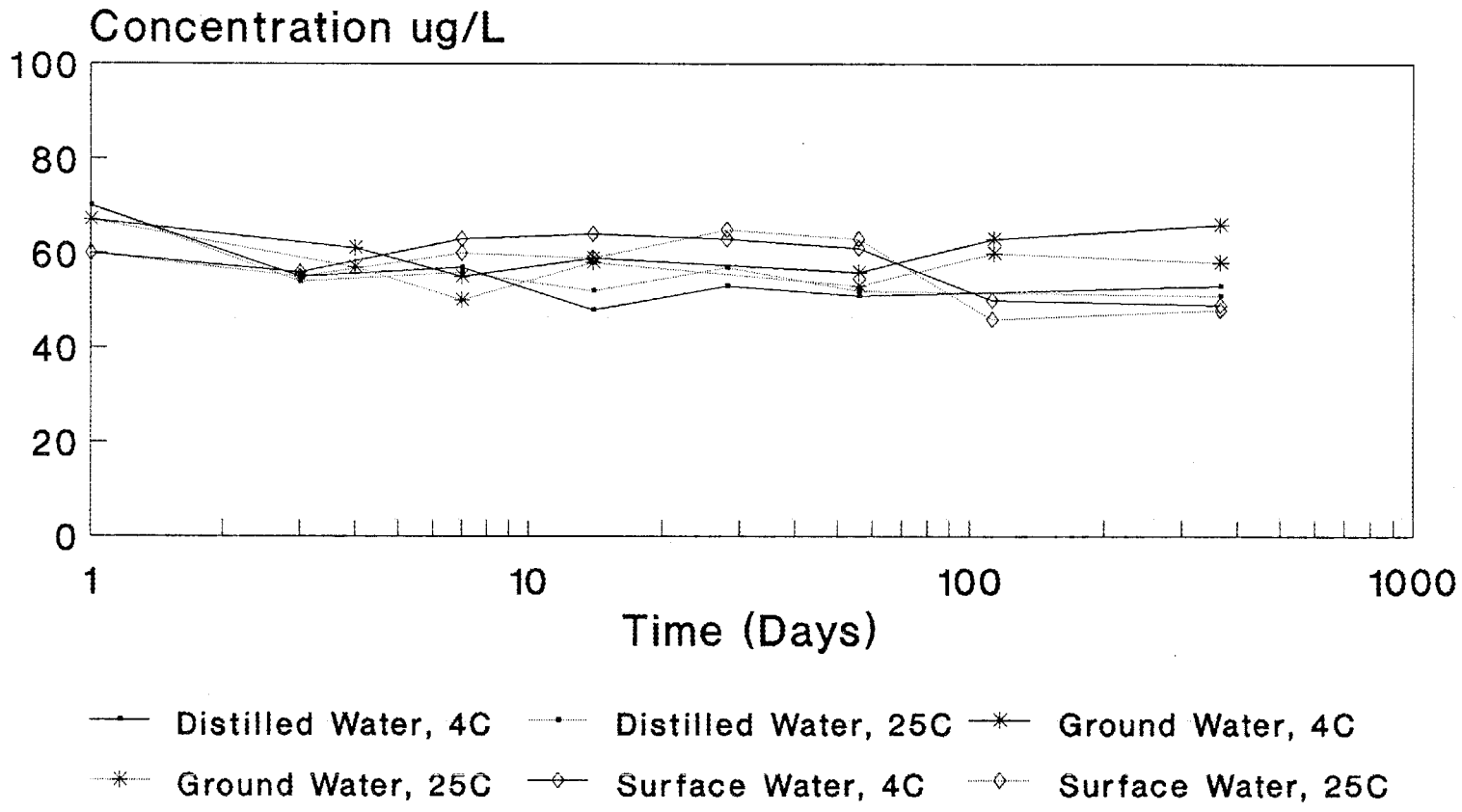
Data for Individual Volatile Organic Compounds

(Low Concentration Level)

Table B.1 Summary Statistics for low level concentrations (μg/L) for <u>Methylene Chloride</u>.

			Days									
			0	3	4	7	14	28	56	112	365	All
Water	Storage											
Distilled	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	69.6	.	.	.	.	.	.	.	.	69.6
		St Dev	0.9	.	.	.	.	.	.	.	.	0.9
	4 C	Num	.	4.0	.	4.0	4.0	2.0	4.0	.	4.0	22.0
		Mean	.	55.5	.	56.6	48.5	52.6	51.4	.	53.5	53.1
		St Dev	.	0.4	.	1.8	2.9	2.2	0.7	.	0.8	3.2
	Room	Num	.	4.0	.	4.0	4.0	3.0	4.0	.	4.0	23.0
		Mean	.	53.9	.	55.8	51.8	56.9	51.8	.	51.3	53.4
		St Dev	.	0.7	.	1.3	1.3	0.5	0.4	.	2.9	2.5
Ground	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	66.6	.	.	.	.	.	.	.	.	66.6
		St Dev	0.9	.	.	.	.	.	.	.	.	0.9
	4 C	Num	.	.	4.0	3.0	4.0	.	4.0	4.0	4.0	23.0
		Mean	.	.	60.9	54.6	58.6	.	55.8	63.4	65.8	60.1
		St Dev	.	.	6.2	2.1	1.1	.	2.0	1.2	1.8	4.8
	Room	Num	.	.	2.0	2.0	4.0	.	4.0	4.0	4.0	20.0
		Mean	.	.	57.2	50.3	57.6	.	52.7	60.2	57.9	56.4
		St Dev	.	.	6.6	1.3	1.9	.	2.5	2.9	1.9	4.1
Surface	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	59.8	.	.	.	.	.	.	.	.	59.8
		St Dev	1.9	.	.	.	.	.	.	.	.	1.9
	4 C	Num	.	4.0	.	4.0	4.0	4.0	3.0	4.0	4.0	27.0
		Mean	.	56.0	.	63.4	63.8	62.9	61.1	49.9	48.5	57.8
		St Dev	.	2.2	.	2.0	1.8	2.9	2.4	2.3	0.9	6.5
	Room	Num	.	4.0	.	4.0	4.0	4.0	5.0	4.0	4.0	29.0
		Mean	.	55.0	.	59.6	58.6	64.5	62.5	46.4	48.3	56.7
		St Dev	.	1.9	.	2.0	3.4	3.5	3.7	1.9	3.3	7.0

Stability of Methylene Chloride in Environmental Water Samples



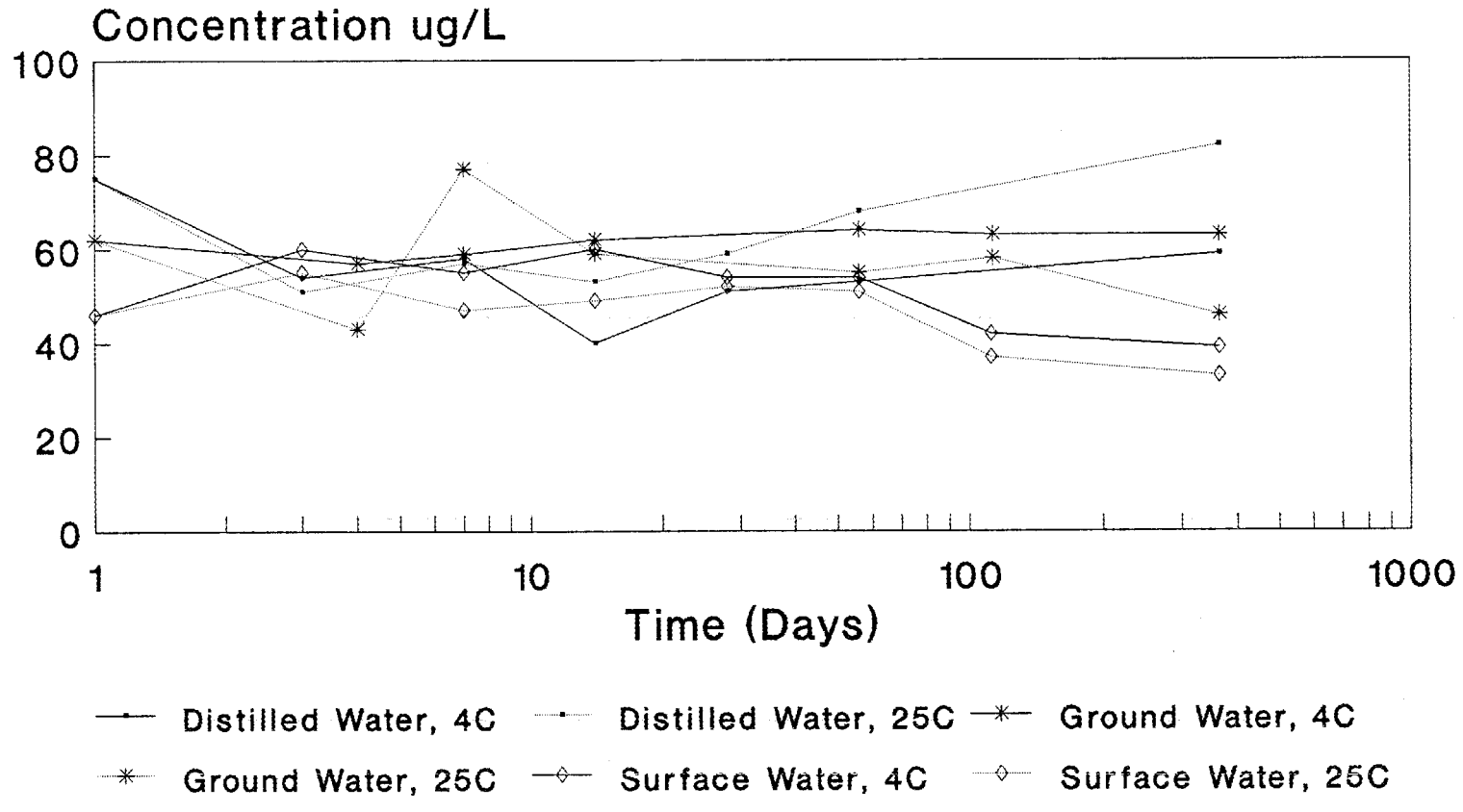
Initial Spike: 50 ug/L

Figure B.1

Table B.2 Summary Statistics for low level concentrations (μg/L) for <u>1,1-Dichloroethylene</u>.

			Days									
			0	3	4	7	14	28	56	112	365	All
Water	Storage											
Distilled	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	74.7	.	.	.	.	.	.	.	.	74.7
		St Dev	3.2	.	.	.	.	.	.	.	.	3.2
	4 C	Num	.	4.0	.	4.0	4.0	2.0	4.0	.	4.0	22.0
		Mean	.	54.0	.	58.0	40.1	51.1	53.4	.	59.1	52.8
		St Dev	.	1.0	.	2.7	4.1	0.7	0.3	.	0.8	6.9
	Room	Num	.	4.0	.	4.0	4.0	3.0	4.0	.	4.0	23.0
		Mean	.	51.1	.	57.4	53.5	59.2	68.4	.	81.9	62.0
		St Dev	.	1.5	.	2.7	4.0	0.4	8.1	.	10.4	12.1
Ground	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	61.9	.	.	.	.	.	.	.	.	61.9
		St Dev	2.3	.	.	.	.	.	.	.	.	2.3
	4 C	Num	.	.	4.0	3.0	4.0	.	4.0	4.0	4.0	23.0
		Mean	.	.	57.1	58.6	61.5	.	63.7	62.7	63.5	61.3
		St Dev	.	.	2.9	3.6	1.4	.	5.2	2.6	2.1	3.8
	Room	Num	.	.	2.0	2.0	4.0	.	4.0	4.0	4.0	20.0
		Mean	.	.	43.0	76.7	59.2	.	55.3	58.2	45.9	55.7
		St Dev	.	.	3.6	4.0	1.5	.	4.8	4.8	5.2	10.0
Surface	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	45.5	.	.	.	.	.	.	.	.	45.5
		St Dev	3.7	.	.	.	.	.	.	.	.	3.7
	4 C	Num	.	4.0	.	4.0	4.0	4.0	3.0	4.0	4.0	27.0
		Mean	.	60.1	.	54.7	59.6	54.2	53.7	41.7	39.4	51.8
		St Dev	.	4.7	.	0.6	2.0	1.7	1.6	2.7	1.1	8.2
	Room	Num	.	4.0	.	4.0	4.0	4.0	5.0	4.0	4.0	29.0
		Mean	.	54.9	.	46.6	48.6	51.6	50.9	37.4	33.4	46.4
		St Dev	.	6.6	.	4.2	6.4	4.7	4.4	1.9	1.9	8.4

1,1-Dichloroethylene in Environmental Water Samples



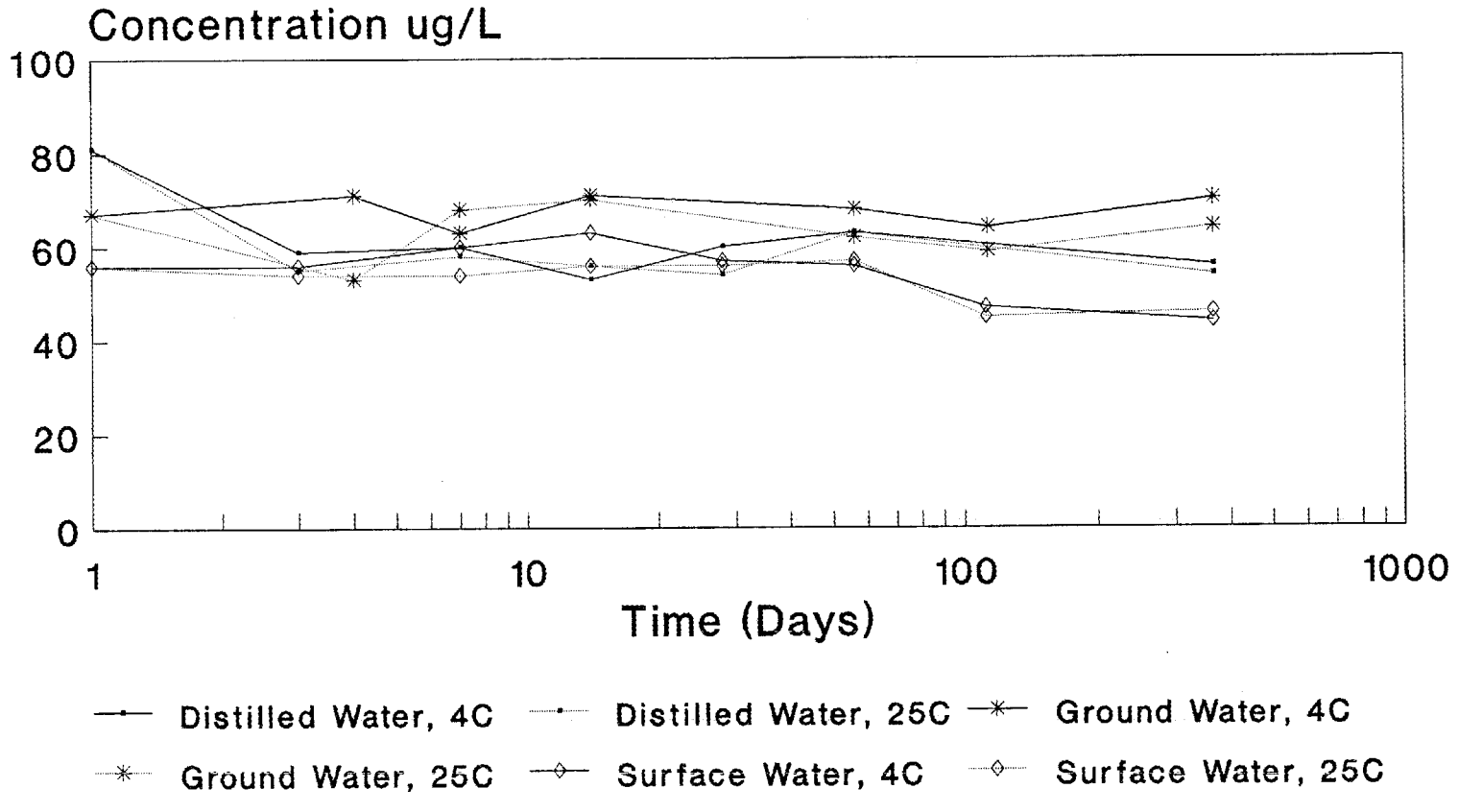
Initial Spike: 50 ug/L

Figure B.2

Table B.3 Summary Statistics for low level concentrations (μg/L) for 1,1-Dichloroethane.

			Days									
			0	3	4	7	14	28	56	112	365	All
Water	Storage											
Distilled	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	81.0	.	.	.	.	.	.	.	.	81.0
		St Dev	2.3	.	.	.	.	.	.	.	.	2.3
	4 C	Num	.	4.0	.	4.0	4.0	2.0	4.0	.	4.0	22.0
		Mean	.	58.7	.	59.9	53.1	60.2	62.6	.	55.8	58.2
		St Dev	.	0.8	.	2.2	2.3	2.6	1.0	.	0.2	3.6
	Room	Num	.	4.0	.	4.0	4.0	3.0	4.0	.	4.0	23.0
		Mean	.	55.1	.	58.4	56.1	53.5	63.2	.	53.8	56.8
		St Dev	.	1.5	.	2.7	3.5	0.6	0.2	.	1.8	3.9
Ground	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	66.7	.	.	.	.	.	.	.	.	66.7
		St Dev	1.9	.	.	.	.	.	.	.	.	1.9
	4 C	Num	.	.	4.0	3.0	4.0	.	4.0	4.0	4.0	23.0
		Mean	.	.	70.6	63.0	70.8	.	67.5	64.0	70.4	67.9
		St Dev	.	.	5.1	8.0	2.4	.	4.7	1.5	2.5	4.9
	Room	Num	.	.	2.0	2.0	4.0	.	4.0	4.0	4.0	20.0
		Mean	.	.	53.4	67.8	69.6	.	62.1	59.3	63.7	63.1
		St Dev	.	.	4.7	4.8	0.8	.	4.5	3.2	2.1	5.7
Surface	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	55.5	.	.	.	.	.	.	.	.	55.5
		St Dev	2.5	.	.	.	.	.	.	.	.	2.5
	4 C	Num	.	4.0	.	4.0	4.0	4.0	3.0	4.0	4.0	27.0
		Mean	.	56.4	.	59.8	62.8	57.4	56.0	47.2	44.0	54.8
		St Dev	.	2.8	.	1.2	1.5	1.8	3.0	1.8	1.4	6.7
	Room	Num	.	4.0	.	4.0	4.0	4.0	5.0	4.0	4.0	29.0
		Mean	.	54.1	.	54.1	55.9	55.8	56.7	45.5	46.0	52.7
		St Dev	.	3.2	.	4.0	3.0	3.5	2.2	1.9	1.8	5.2

Stability of 1,1-Dichloroethane in Environmental Water Samples



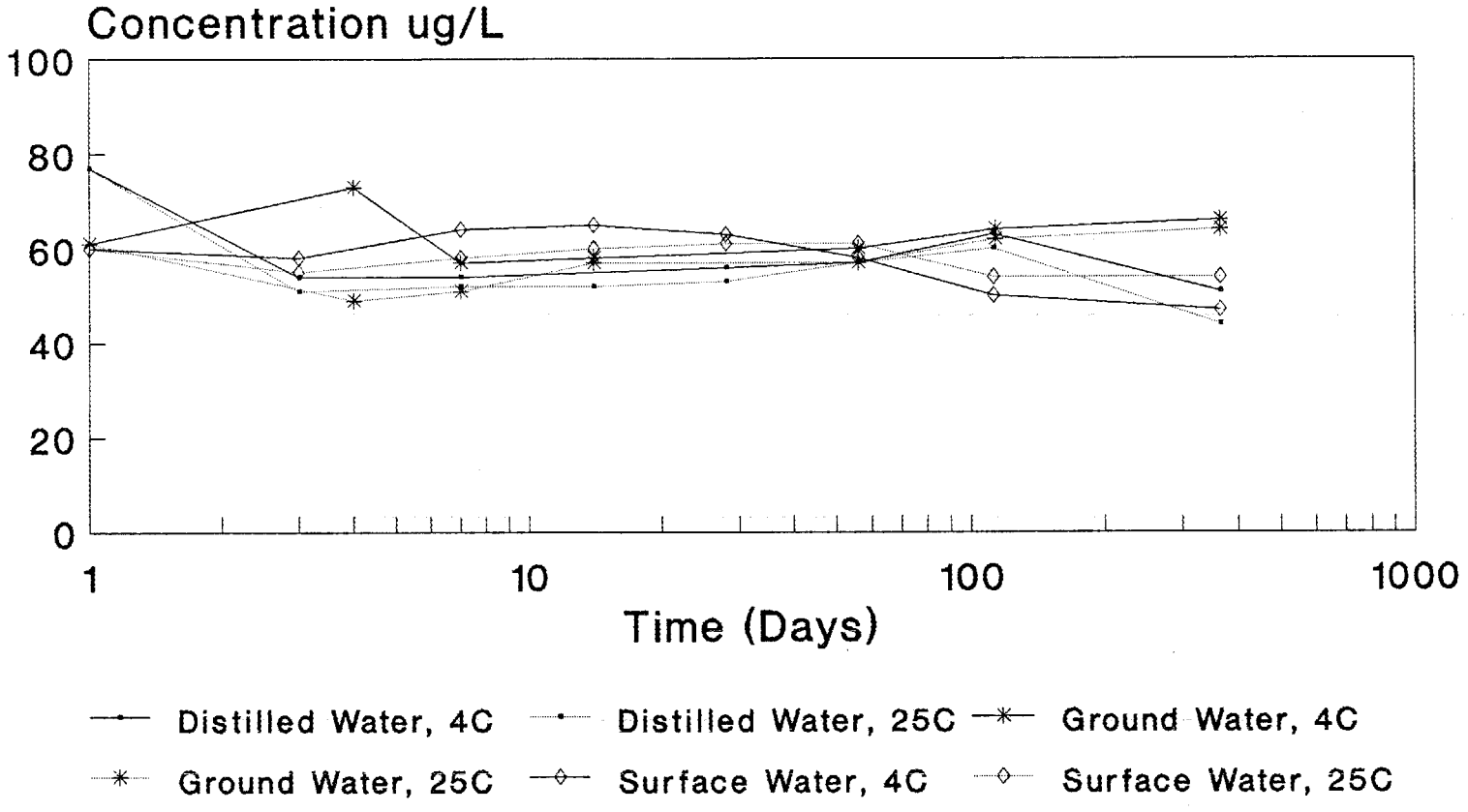
Initial Spike: 50 ug/L

Figure B.3

Table B.4 Summary Statistics for low level concentrations (μg/L) for Chloroform.

			Days									
			0	3	4	7	14	28	56	112	365	All
Water	Storage											
Distilled	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	76.6	.	.	.	.	.	.	.	.	76.6
		St Dev	1.9	.	.	.	.	.	.	.	.	1.9
	4 C	Num	.	4.0	.	4.0	.	2.0	4.0	4.0	4.0	22.0
		Mean	.	54.0	.	54.1	.	56.5	56.9	63.2	51.0	55.9
		St Dev	.	1.1	.	1.8	.	2.6	0.3	1.7	0.4	4.2
	Room	Num	.	4.0	.	4.0	4.0	3.0	4.0	4.0	4.0	27.0
		Mean	.	51.1	.	52.4	51.6	53.3	57.0	60.3	43.7	52.8
		St Dev	.	1.8	.	2.7	3.3	1.1	1.0	3.1	1.3	5.3
Ground	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	61.3	.	.	.	.	.	.	.	.	61.3
		St Dev	1.3	.	.	.	.	.	.	.	.	1.3
	4 C	Num	.	.	4.0	3.0	4.0	.	4.0	4.0	4.0	23.0
		Mean	.	.	73.0	56.8	58.0	.	59.8	64.4	66.0	63.3
		St Dev	.	.	4.2	1.5	1.7	.	1.9	2.0	3.6	6.1
	Room	Num	.	.	2.0	2.0	4.0	.	4.0	4.0	4.0	20.0
		Mean	.	.	48.8	50.7	57.5	.	57.4	61.8	63.8	58.0
		St Dev	.	.	6.5	3.3	0.5	.	1.1	4.1	4.6	5.8
Surface	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	59.7	.	.	.	.	.	.	.	.	59.7
		St Dev	2.7	.	.	.	.	.	.	.	.	2.7
	4 C	Num	.	4.0	.	4.0	4.0	4.0	3.0	4.0	4.0	27.0
		Mean	.	57.7	.	63.8	65.5	63.0	57.9	50.5	46.9	57.9
		St Dev	.	4.0	.	1.0	2.3	2.1	1.5	1.4	1.4	7.0
	Room	Num	.	4.0	.	4.0	4.0	4.0	5.0	4.0	4.0	29.0
		Mean	.	54.8	.	57.7	59.8	61.4	61.1	53.5	54.4	57.7
		St Dev	.	2.3	.	3.1	3.7	3.3	3.6	1.5	3.3	4.2

Stability of Chloroform in Environmental Water Samples



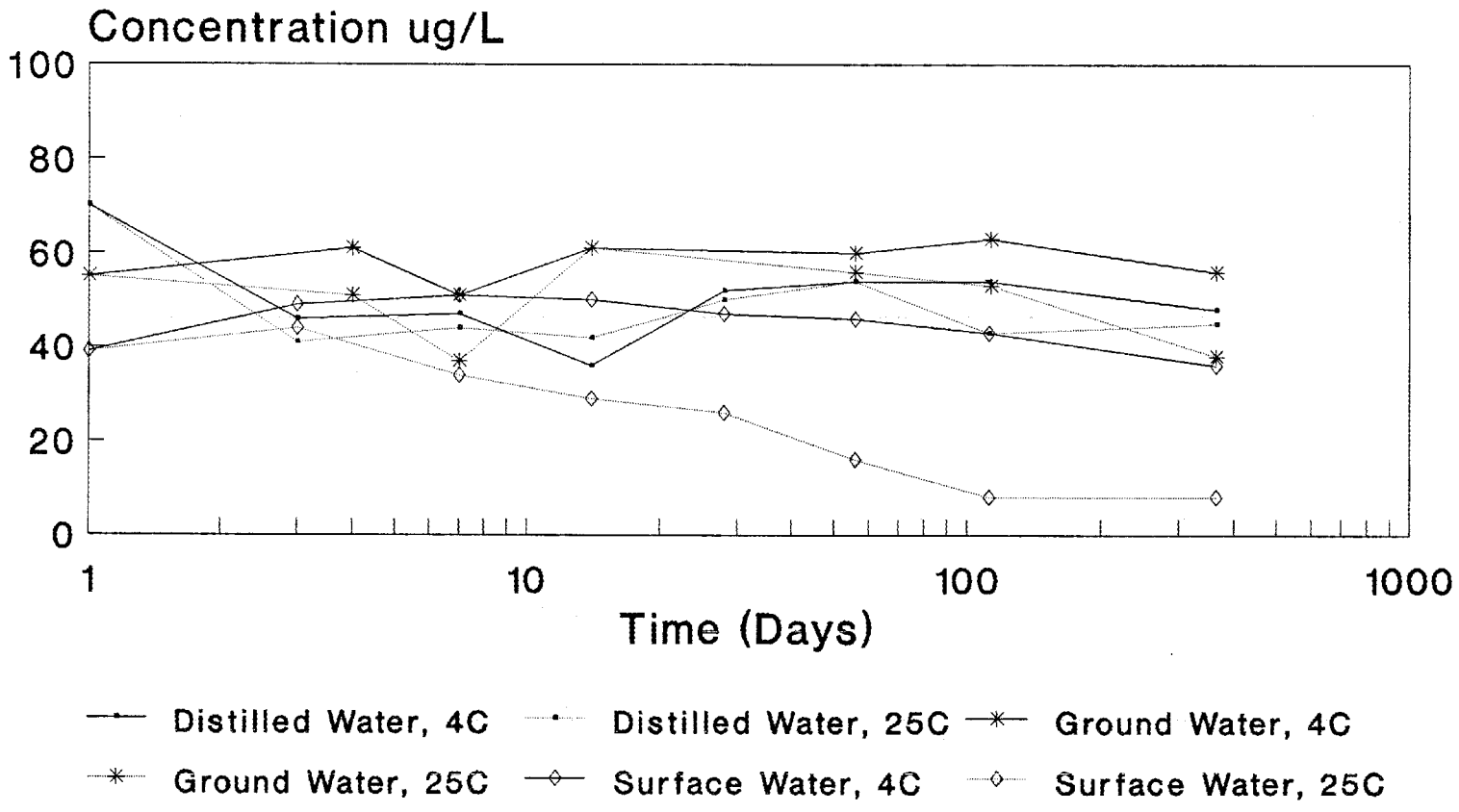
Initial Spike: 50 ug/L

Figure B.4

Table B.5 Summary Statistics for low level concentrations (μg/L) for Carbon Tetrachloride.

Water	Storage		Days 0	3	4	7	14	28	56	112	365	All
Distilled	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	70.0	.	.	.	.	.	.	.	.	70.0
		St Dev	3.5	.	.	.	.	.	.	.	.	3.5
	4 C	Num	.	4.0	.	4.0	4.0	2.0	4.0	4.0	4.0	26.0
		Mean	.	46.2	.	47.0	36.1	52.4	54.1	54.5	48.0	48.0
		St Dev	.	1.3	.	2.3	2.6	1.2	0.7	2.4	0.4	6.3
	Room	Num	.	4.0	.	4.0	4.0	3.0	4.0	4.0	4.0	27.0
		Mean	.	40.7	.	44.0	42.0	50.4	53.9	43.4	44.9	45.4
		St Dev	.	3.2	.	5.0	6.2	1.3	0.5	4.3	2.4	5.6
Ground	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	54.9	.	.	.	.	.	.	.	.	54.9
		St Dev	3.1	.	.	.	.	.	.	.	.	3.1
	4 C	Num	.	.	4.0	3.0	4.0	.	4.0	4.0	4.0	23.0
		Mean	.	.	61.5	50.6	60.9	.	59.8	62.7	55.5	58.8
		St Dev	.	.	6.7	2.8	1.4	.	2.6	1.7	1.6	5.0
	Room	Num	.	.	2.0	2.0	4.0	.	3.0	4.0	4.0	19.0
		Mean	.	.	50.9	36.8	60.8	.	56.5	52.9	38.0	50.1
		St Dev	.	.	13.6	1.5	1.8	.	0.7	5.0	7.0	10.5
Surface	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	39.3	.	.	.	.	.	.	.	.	39.3
		St Dev	3.8	.	.	.	.	.	.	.	.	3.8
	4 C	Num	.	4.0	.	4.0	4.0	4.0	3.0	4.0	4.0	27.0
		Mean	.	49.4	.	50.8	50.0	46.6	45.8	42.8	36.1	45.9
		St Dev	.	5.7	.	1.5	3.0	2.2	1.8	2.2	1.2	5.6
	Room	Num	.	4.0	.	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Mean	.	43.8	.	34.0	28.7	26.4	15.9	8.1	7.6	23.5
		St Dev	.	6.7	.	3.7	4.3	3.7	2.1	5.4	8.7	13.6

Stability of Carbon Tetrachloride in Environmental Water Samples



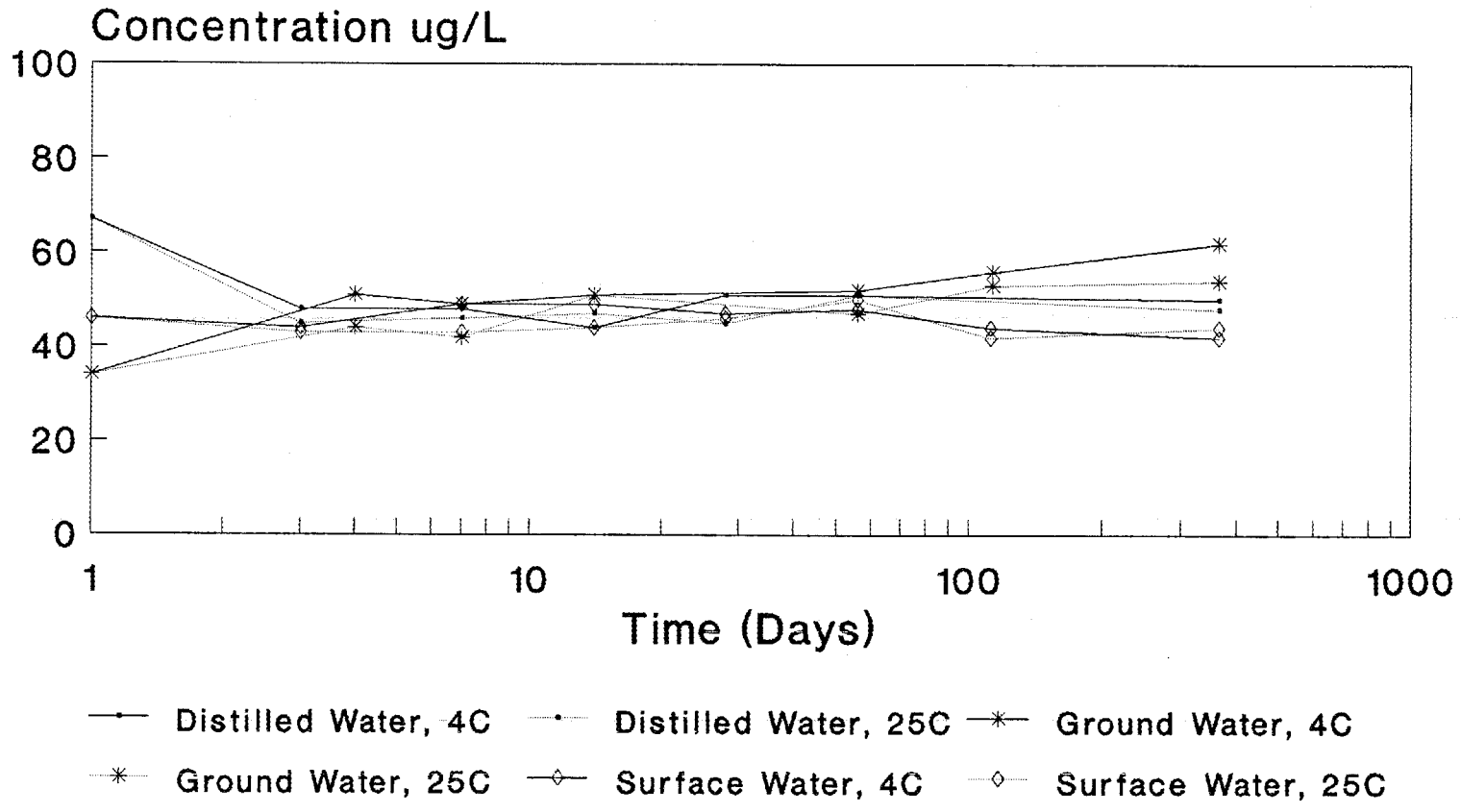
Initial Spike: 50 ug/L

Figure B.5

Table B.6 Summary Statistics for low level concentrations ($\mu g/L$) for <u>1,2-Dichloropropane</u>.

			Days									
			0	3	4	7	14	28	56	112	365	All
Water	Storage											
Distilled	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	67.3	.	.	.	.	.	.	.	.	67.3
		St Dev	1.8	.	.	.	.	.	.	.	.	1.8
	4 C	Num	.	4.0	.	4.0	4.0	2.0	4.0	.	4.0	22.0
		Mean	.	48.0	.	47.9	44.3	50.8	50.8	.	49.9	48.4
		St Dev	.	0.8	.	1.7	2.1	1.6	0.1	.	0.8	2.6
	Room	Num	.	4.0	.	4.0	4.0	3.0	4.0	.	4.0	23.0
		Mean	.	44.8	.	46.2	46.6	44.8	50.9	.	47.9	46.9
		St Dev	.	1.6	.	3.4	2.7	0.9	1.2	.	1.1	2.8
Ground	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	33.7	.	.	.	.	.	.	.	.	33.7
		St Dev	0.9	.	.	.	.	.	.	.	.	0.9
	4 C	Num	.	.	4.0	3.0	4.0	.	4.0	4.0	4.0	23.0
		Mean	.	.	50.7	48.7	51.2	.	51.5	55.8	62.2	53.6
		St Dev	.	.	2.7	2.0	1.8	.	2.1	0.6	2.7	4.9
	Room	Num	.	.	2.0	2.0	4.0	.	4.0	4.0	4.0	20.0
		Mean	.	.	43.9	42.0	51.2	.	47.3	52.7	54.4	49.7
		St Dev	.	.	8.6	3.1	0.5	.	2.7	2.7	2.3	5.1
Surface	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	46.1	.	.	.	.	.	.	.	.	46.1
		St Dev	2.1	.	.	.	.	.	.	.	.	2.1
	4 C	Num	.	4.0	.	4.0	4.0	4.0	3.0	4.0	4.0	27.0
		Mean	.	44.5	.	49.4	49.1	47.5	47.6	43.9	41.8	46.2
		St Dev	.	1.8	.	1.0	0.9	1.5	1.0	1.1	0.8	3.0
	Room	Num	.	4.0	.	4.0	4.0	4.0	5.0	4.0	4.0	29.0
		Mean	.	43.0	.	43.3	44.5	46.2	50.4	41.8	43.7	44.9
		St Dev	.	1.9	.	3.6	2.3	3.0	2.4	1.4	1.3	3.6

Stability of 1,2-Dichloropropane in Environmental Water Samples



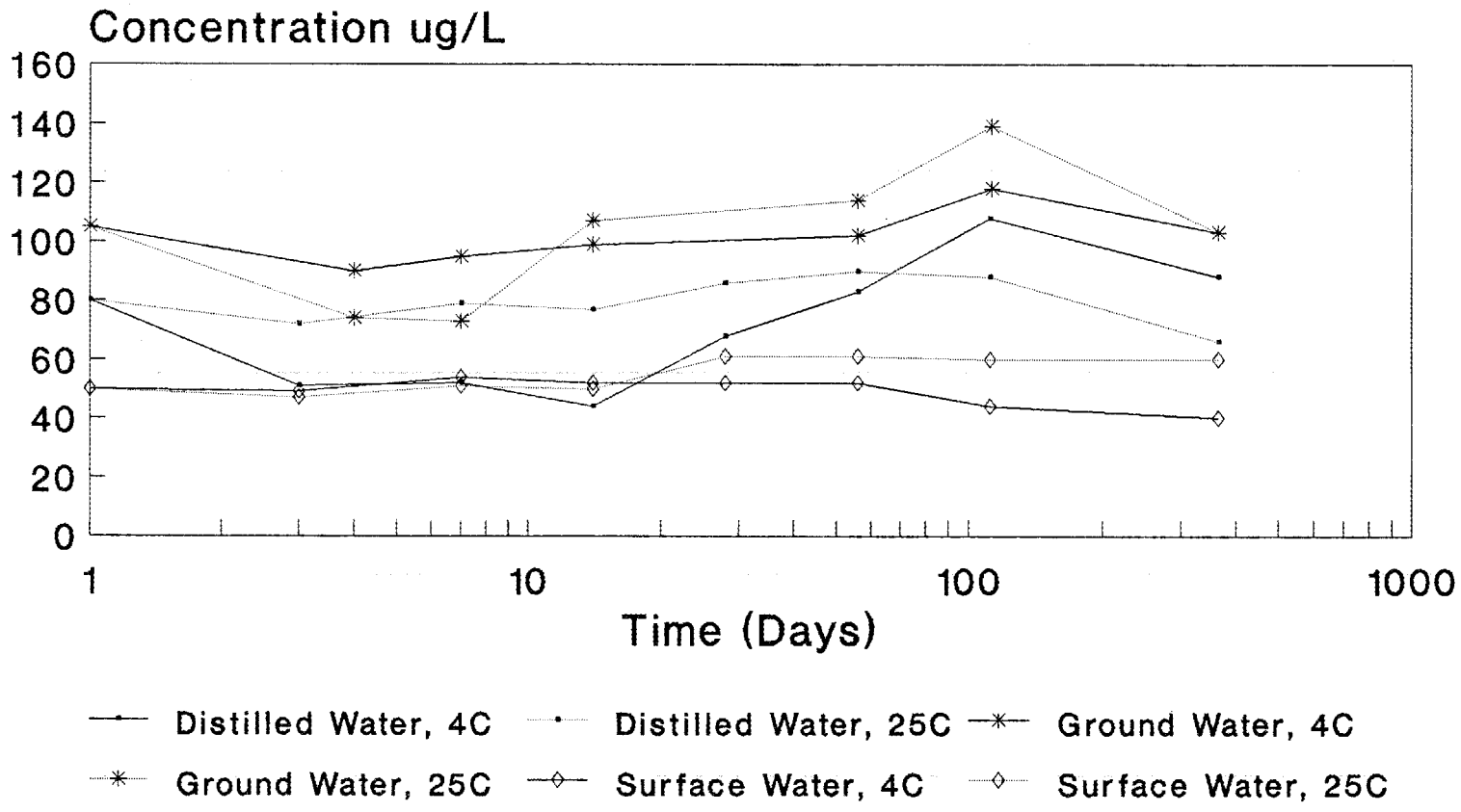
Initial Spike: 50 ug/L

Figure B.6

Table B.7 Summary Statistics for low level concentrations (μg/L) for Trichloroethylene.

Water	Storage		Days 0	3	4	7	14	28	56	112	365	All
Distilled	None	Num	3.0	.	.	.	.	.	.	.	.	3.0
		Mean	79.7	.	.	.	.	.	.	.	.	79.7
		St Dev	6.4	.	.	.	.	.	.	.	.	6.4
	4 C	Num	.	4.0	.	3.0	4.0	2.0	4.0	4.0	4.0	25.0
		Mean	.	50.7	.	52.4	43.6	68.0	82.9	108	87.5	71.4
		St Dev	.	2.1	.	3.0	3.0	1.3	1.0	5.7	1.3	23.4
	Room	Num	.	4.0	.	4.0	4.0	3.0	4.0	4.0	4.0	27.0
		Mean	.	72.3	.	79.2	76.6	85.8	89.9	88.3	65.6	79.4
		St Dev	.	5.0	.	9.1	11.4	1.9	0.7	7.2	9.4	10.8
Ground	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	105	.	.	.	.	.	.	.	.	105
		St Dev	4.0	.	.	.	.	.	.	.	.	4.0
	4 C	Num	.	.	4.0	3.0	4.0	.	4.0	4.0	4.0	23.0
		Mean	.	.	89.9	94.6	99.4	.	102	118	103	101
		St Dev	.	.	4.5	7.7	2.5	.	6.4	2.6	3.5	10.0
	Room	Num	.	.	2.0	2.0	4.0	.	3.0	4.0	4.0	19.0
		Mean	.	.	74.4	73.0	107	.	114	139	103	107
		St Dev	.	.	17.9	3.9	2.5	.	1.6	11.7	12.3	23.6
Surface	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	50.0	.	.	.	.	.	.	.	.	50.0
		St Dev	2.3	.	.	.	.	.	.	.	.	2.3
	4 C	Num	.	4.0	.	4.0	4.0	4.0	3.0	4.0	4.0	27.0
		Mean	.	49.3	.	53.7	51.8	51.5	51.6	44.4	40.5	48.9
		St Dev	.	1.9	.	2.0	1.1	3.6	2.1	2.1	0.8	4.9
	Room	Num	.	4.0	.	4.0	4.0	4.0	5.0	4.0	4.0	29.0
		Mean	.	47.5	.	50.7	49.7	61.1	60.7	60.0	59.8	55.8
		St Dev	.	4.2	.	4.2	5.2	9.5	8.4	3.4	3.8	7.8

Stability of Trichloroethylene in Environmental Water Samples



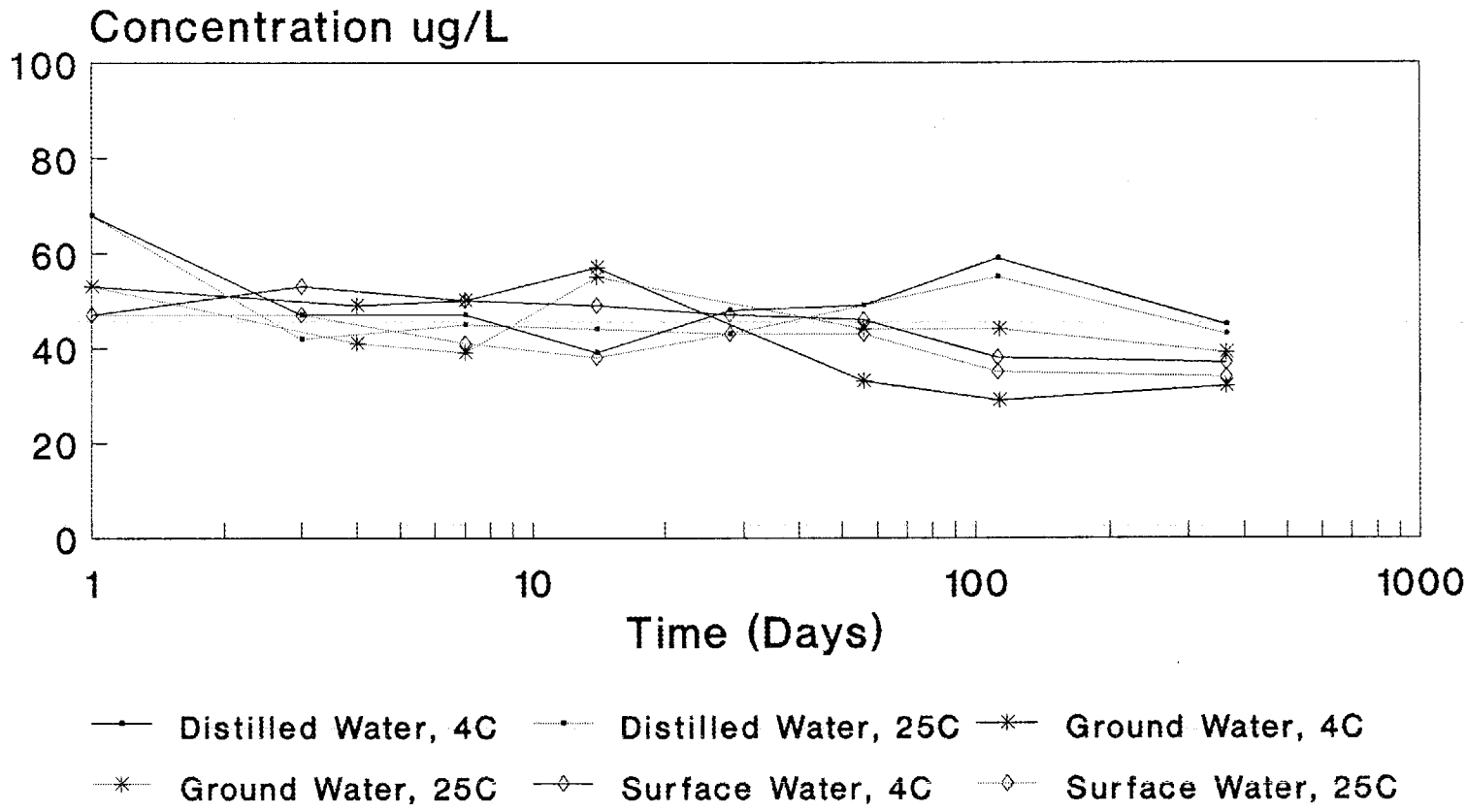
Initial Spike: 50 ug/L

Figure B.7

Table B.8 Summary Statistics for low level concentrations (μg/L) for Benzene.

Water	Storage		Days 0	3	4	7	14	28	56	112	365	All
Distilled	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	68.1	.	.	.	.	.	.	.	.	68.1
		St Dev	1.8	.	.	.	.	.	.	.	.	1.8
	4 C	Num	.	4.0	.	4.0	4.0	2.0	4.0	4.0	4.0	26.0
		Mean	.	46.7	.	47.5	39.3	47.7	48.7	58.8	45.1	47.7
		St Dev	.	1.3	.	1.9	2.6	2.1	0.5	0.6	0.7	5.9
	Room	Num	.	4.0	.	4.0	4.0	3.0	4.0	4.0	4.0	27.0
		Mean	.	42.1	.	45.1	43.7	42.6	48.9	55.3	42.7	45.9
		St Dev	.	2.0	.	3.8	3.9	0.8	0.6	2.3	2.1	5.1
Ground	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	53.4	.	.	.	.	.	.	.	.	53.4
		St Dev	2.1	.	.	.	.	.	.	.	.	2.1
	4 C	Num	.	.	4.0	3.0	4.0	.	4.0	4.0	4.0	23.0
		Mean	.	.	49.2	49.8	57.1	.	32.7	28.9	31.7	41.2
		St Dev	.	.	2.9	2.3	1.7	.	3.0	0.6	3.1	11.4
	Room	Num	.	.	2.0	2.0	4.0	.	3.0	4.0	2.0	17.0
		Mean	.	.	40.5	38.6	54.6	.	43.5	43.8	39.2	44.7
		St Dev	.	.	9.1	2.8	1.3	.	4.2	3.3	1.3	6.8
Surface	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	46.6	.	.	.	.	.	.	.	.	46.6
		St Dev	2.7	.	.	.	.	.	.	.	.	2.7
	4 C	Num	.	4.0	.	4.0	4.0	4.0	3.0	4.0	4.0	27.0
		Mean	.	53.0	.	49.6	49.3	46.8	45.7	38.1	37.2	45.7
		St Dev	.	3.4	.	0.8	0.7	1.8	1.7	1.6	0.9	5.9
	Room	Num	.	4.0	.	4.0	4.0	4.0	5.0	4.0	2.0	27.0
		Mean	.	46.5	.	40.8	38.2	42.6	43.0	34.7	34.3	40.6
		St Dev	.	3.8	.	3.0	2.7	4.3	1.7	1.6	3.4	4.8

Stability of Benzene in Environmental Water Samples



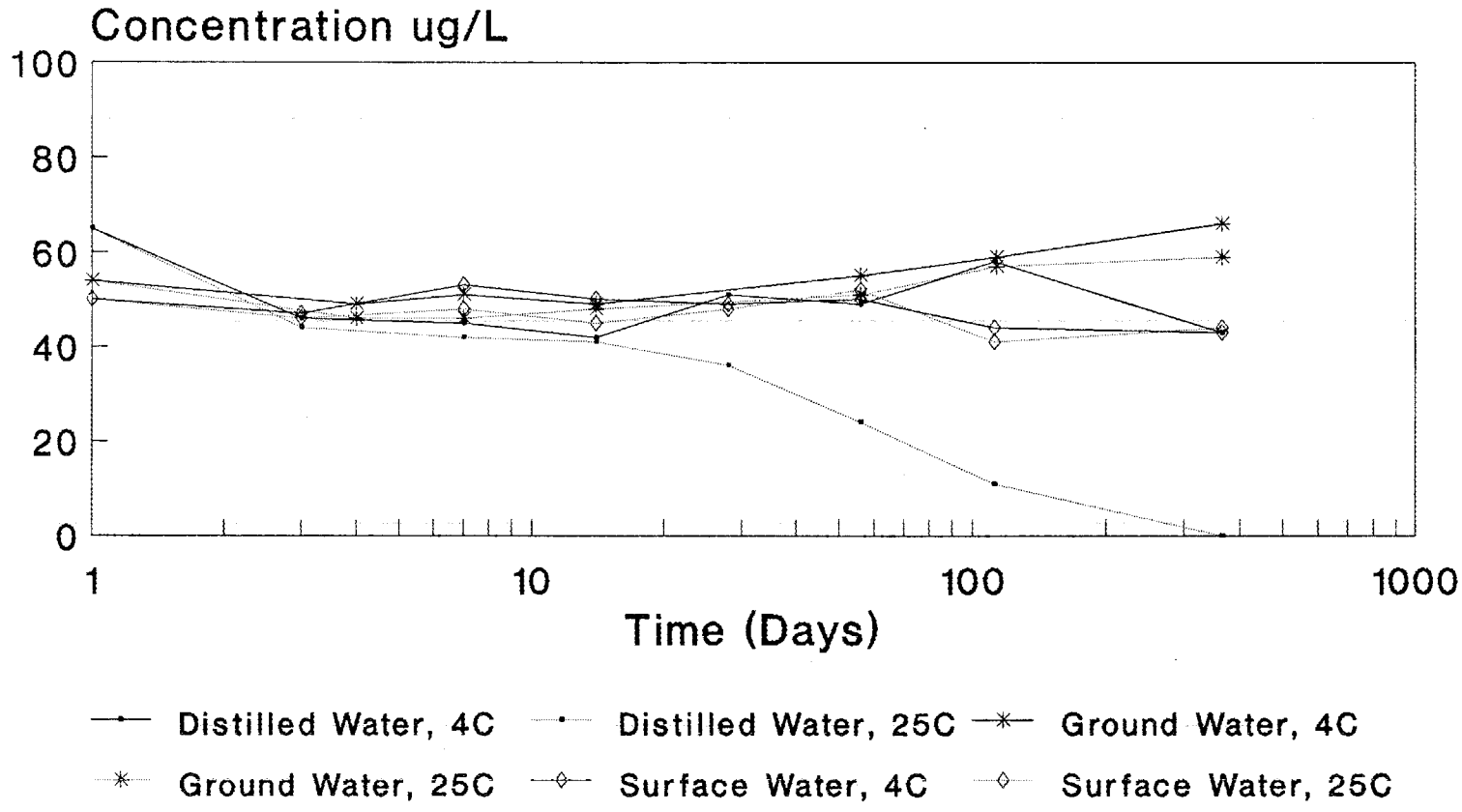
Initial Spike: 50 ug/L

Figure B.8

Table B.9 Summary Statistics for low level concentrations (μg/L) for 1,1,2-Trichloroethane.

			Days									
			0	3	4	7	14	28	56	112	365	All
Water	Storage											
Distilled	None	Num	4.0	.	.	.	.	.	.	.		4.0
		Mean	65.4	.	.	.	.	.	.	.	.	65.4
		St Dev	1.1	.	.	.	.	.	.	.	.	1.1
	4 C	Num	.	4.0	.	4.0	4.0	2.0	4.0	4.0	4.0	26.0
		Mean	.	46.4	.	45.4	41.8	51.1	49.5	58.2	43.1	47.7
		St Dev	.	1.0	.	1.3	2.2	2.1	0.5	0.9	0.8	5.5
	Room	Num	.	4.0	.	4.0	4.0	3.0	3.0	3.0	4.0	25.0
		Mean	.	43.9	.	42.4	40.7	36.3	23.5	11.2	0.3	28.9
		St Dev	.	1.2	.	2.1	1.9	0.6	0.8	1.6	0.2	16.7
Ground	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	54.1	.	.	.	.	.	.	.	.	54.1
		St Dev	1.4	.	.	.	.	.	.	.	.	1.4
	4 C	Num	.	.	4.0	3.0	4.0	.	4.0	4.0	4.0	23.0
		Mean	.	.	49.0	50.7	49.0	.	54.9	59.2	65.6	54.9
		St Dev	.	.	1.2	1.8	0.9	.	1.2	1.5	2.0	6.4
	Room	Num	.	.	2.0	2.0	4.0	.	4.0	4.0	4.0	20.0
		Mean	.	.	46.1	46.0	48.3	.	51.2	56.9	58.9	52.3
		St Dev	.	.	8.2	2.7	1.3	.	1.6	2.8	1.5	5.6
Surface	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	49.6	.	.	.	.	.	.	.	.	49.6
		St Dev	2.4	.	.	.	.	.	.	.	.	2.4
	4 C	Num	.	4.0	.	4.0	4.0	4.0	3.0	4.0	4.0	27.0
		Mean	.	46.5	.	52.6	49.7	49.2	50.3	44.0	43.3	47.9
		St Dev	.	1.4	.	0.5	1.2	1.9	2.2	1.1	0.8	3.5
	Room	Num	.	4.0	.	4.0	4.0	4.0	5.0	4.0	4.0	29.0
		Mean	.	45.8	.	48.0	45.2	48.2	51.5	41.3	43.7	46.4
		St Dev	.	1.7	.	2.7	1.6	2.4	2.3	1.9	1.8	3.7

Stability of 1,1,2-Trichloroethane in Environmental Water Samples



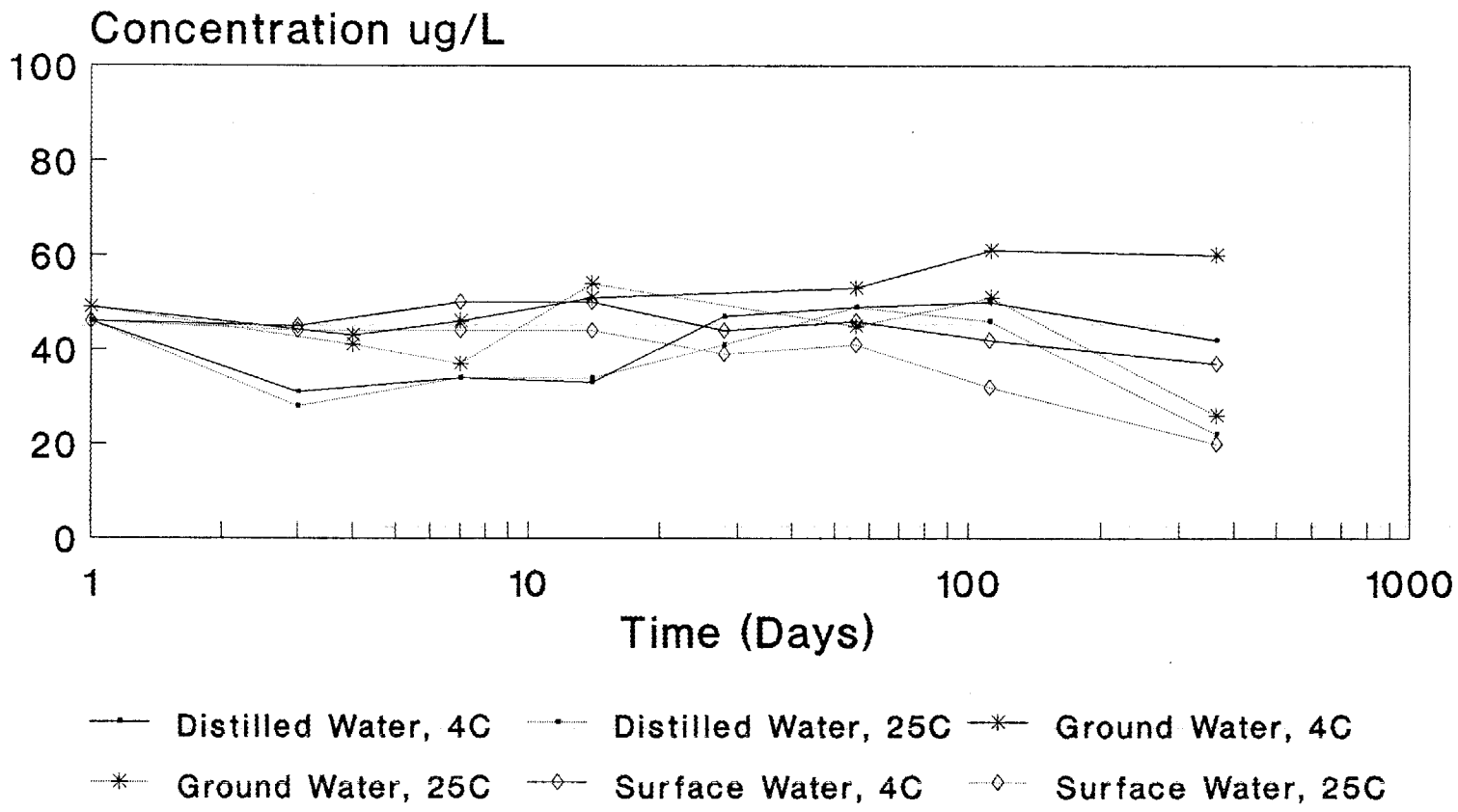
Initial Spike: 50 ug/L

Figure B.9

Table B.10 Summary Statistics for low level concentrations (μg/L) for <u>Bromoform</u>.

Water	Storage		Days 0	3	4	7	14	28	56	112	365	All
Distilled	None	Num	4.0	.	.	.	.	.	.	.		4.0
		Mean	45.9	.	.	.	.	.	.	.		45.9
		St Dev	3.7	.	.	.	.	.	.	.		3.7
	4 C	Num	.	4.0	.	4.0	4.0	2.0	4.0	4.0	4.0	26.0
		Mean	.	30.7	.	34.2	32.6	46.5	48.7	50.4	41.9	40.3
		St Dev	.	1.8	.	1.3	2.5	2.2	1.3	2.2	0.7	8.0
	Room	Num	.	4.0	.	4.0	4.0	3.0	4.0	4.0	4.0	27.0
		Mean	.	27.5	.	33.9	34.5	41.0	49.4	46.3	21.5	36.1
		St Dev	.	2.1	.	3.0	2.9	1.4	1.9	3.5	1.1	9.8
Ground	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	48.6	.	.	.	.	.	.	.	.	48.6
		St Dev	1.9	.	.	.	.	.	.	.	.	1.9
	4 C	Num	.	.	4.0	3.0	4.0	.	4.0	4.0	4.0	23.0
		Mean	.	.	42.6	46.2	51.3	.	52.6	61.0	59.9	52.5
		St Dev	.	.	2.5	1.6	0.7	.	1.0	2.6	1.2	7.0
	Room	Num	.	.	2.0	2.0	4.0	.	4.0	4.0	4.0	20.0
		Mean	.	.	40.8	37.3	53.5	.	44.7	50.6	25.6	42.7
		St Dev	.	.	12.3	3.3	2.1	.	1.2	1.5	5.6	10.9
Surface	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	45.7	.	.	.	.	.	.	.	.	45.7
		St Dev	1.1	.	.	.	.	.	.	.	.	1.1
	4 C	Num	.	4.0	.	4.0	4.0	4.0	3.0	4.0	4.0	27.0
		Mean	.	44.9	.	50.5	50.2	44.3	45.5	42.5	36.7	44.9
		St Dev	.	1.6	.	0.8	1.6	1.8	1.5	0.9	0.9	4.7
	Room	Num	.	4.0	.	4.0	4.0	4.0	5.0	4.0	4.0	29.0
		Mean	.	43.9	.	43.6	43.6	38.9	40.7	31.5	20.0	37.6
		St Dev	.	2.3	.	2.5	1.5	2.5	3.4	1.8	3.9	8.6

Stability of Bromoform in Environmental Water Samples



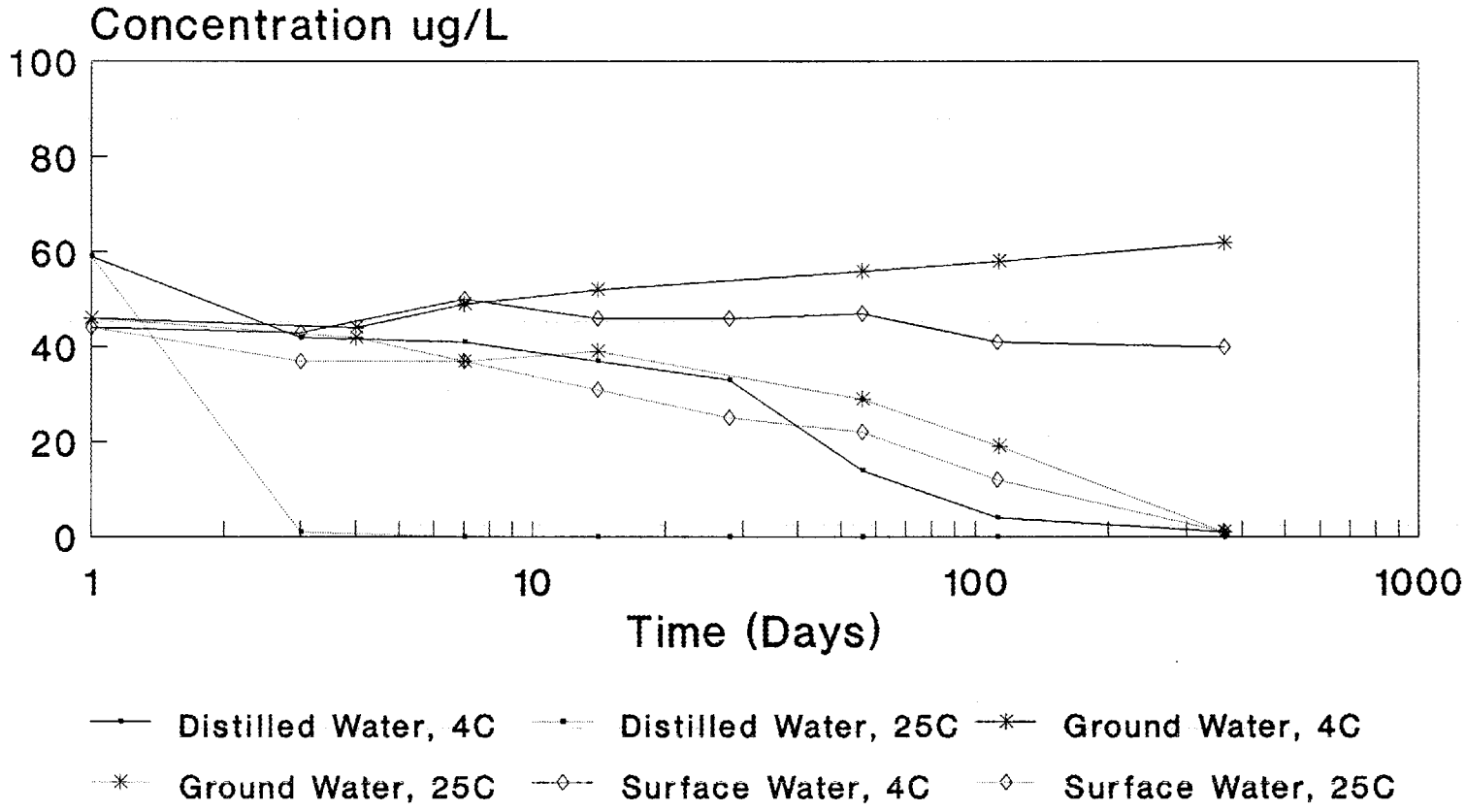
Initial Spike: 50 ug/L

Figure B.10

Table B.11 Summary Statistics for low level concentrations (μg/L) for 1,1,2,2-Tetrachloroethane.

			Days									
			0	3	4	7	14	28	56	112	365	All
Water	Storage											
Distilled	None	Num	3.0	.	.	.	.	.	.	.	.	3.0
		Mean	58.7	.	.	.	.	.	.	.	.	58.7
		St Dev	2.5	.	.	.	.	.	.	.	.	2.5
	4 C	Num	.	4.0	.	3.0	4.0	2.0	4.0	4.0	4.0	25.0
		Mean	.	41.6	.	41.5	37.2	32.6	14.0	3.5	0.6	23.1
		St Dev	.	1.7	.	0.5	3.1	2.1	0.7	1.2	0.0	17.4
	Room	Num	.	4.0	.	4.0	4.0	3.0	4.0	3.0	4.0	26.0
		Mean	.	1.1	.	0.1	0.1	0.2	0.3	0.0	0.4	0.3
		St Dev	.	0.9	.	0.1	0.2	0.2	0.2	0.0	0.1	0.5
Ground	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	46.2	.	.	.	.	.	.	.	.	46.2
		St Dev	8.5	.	.	.	.	.	.	.	.	8.5
	4 C	Num	.	.	4.0	4.0	4.0	.	4.0	4.0	4.0	24.0
		Mean	.	.	44.4	49.2	51.6	.	55.7	57.9	61.7	53.4
		St Dev	.	.	6.7	1.7	1.3	.	1.0	1.7	2.5	6.5
	Room	Num	.	.	2.0	3.0	4.0	.	3.0	4.0	4.0	20.0
		Mean	.	.	41.8	37.4	39.2	.	28.7	18.9	0.7	25.9
		St Dev	.	.	9.2	1.9	2.5	.	2.7	2.3	0.2	15.4
Surface	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	44.4	.	.	.	.	.	.	.	.	44.4
		St Dev	6.0	.	.	.	.	.	.	.	.	6.0
	4 C	Num	.	4.0	.	4.0	4.0	4.0	3.0	4.0	4.0	27.0
		Mean	.	42.7	.	49.6	46.1	46.1	46.6	41.4	40.1	44.6
		St Dev	.	6.7	.	6.7	5.2	2.3	4.0	0.7	0.4	5.1
	Room	Num	.	4.0	.	4.0	4.0	4.0	4.0	4.0	4.0	28.0
		Mean	.	37.4	.	36.8	31.3	24.8	22.5	12.1	1.0	23.7
		St Dev	.	1.2	.	2.6	1.0	0.9	1.8	0.7	0.4	12.7

Stability of 1,1,2,2-Tetrachloroethane in Environmental Water Samples



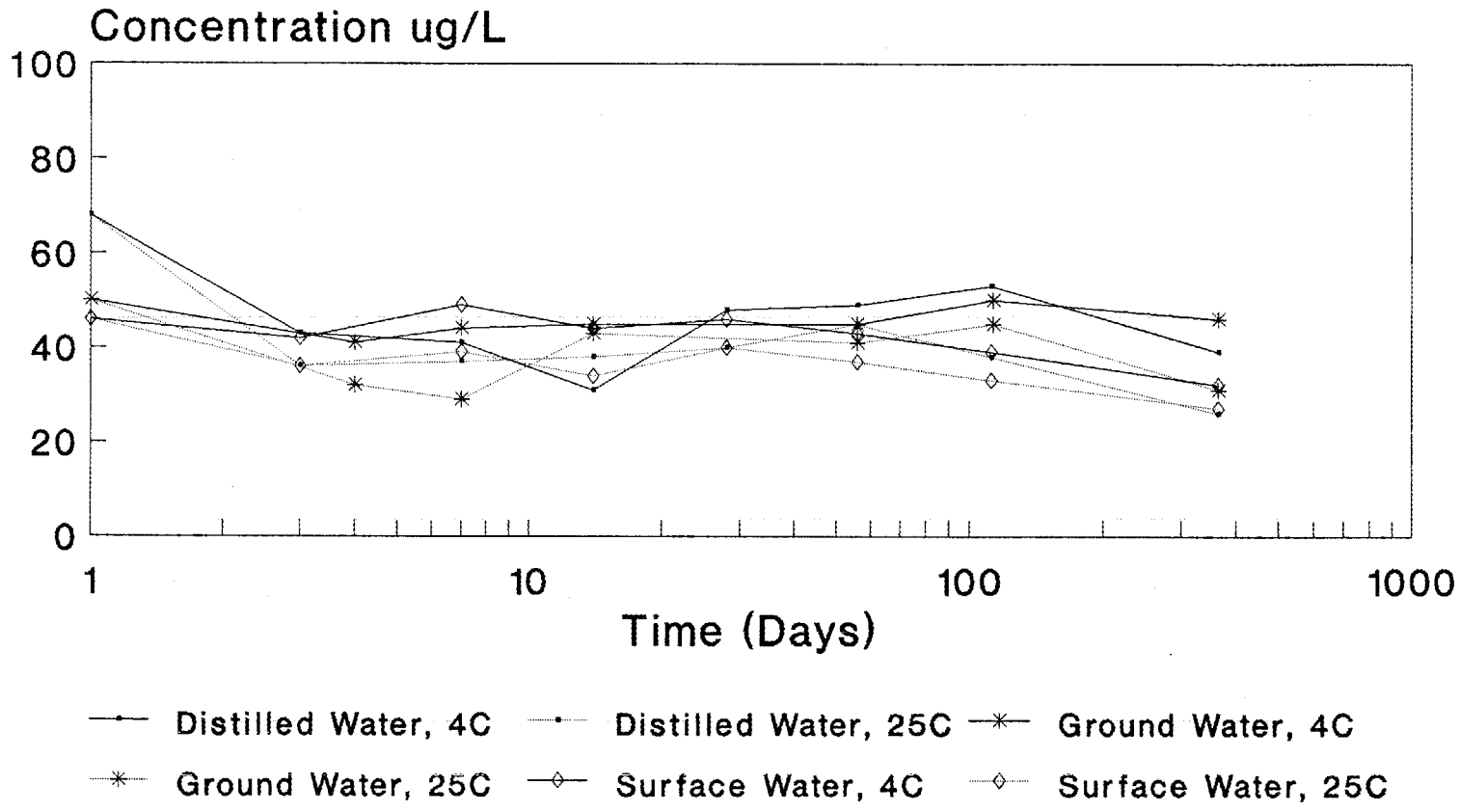
Initial Spike: 50 ug/L

Figure B.11

Table B.12 Summary Statistics for low level concentrations (μg/L) for Tetrachloroethylene.

Water	Storage		Days 0	3	4	7	14	28	56	112	365	All
Distilled	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	68.5	.	.	.	.	.	.	.	.	68.5
		St Dev	2.8	.	.	.	.	.	.	.	.	2.8
	4 C	Num	.	4.0	.	4.0	4.0	2.0	4.0	4.0	4.0	26.0
		Mean	.	42.8	.	40.9	31.0	47.6	48.7	53.3	39.4	43.1
		St Dev	.	1.6	.	2.2	2.1	2.6	0.5	3.8	1.0	7.3
	Room	Num	.	4.0	.	4.0	4.0	3.0	4.0	4.0	4.0	27.0
		Mean	.	36.0	.	36.8	38.1	40.3	45.2	38.4	26.1	37.1
		St Dev	.	2.7	.	5.4	6.8	0.8	1.1	4.7	5.4	6.8
Ground	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	50.2	.	.	.	.	.	.	.	.	50.2
		St Dev	4.1	.	.	.	.	.	.	.	.	4.1
	4 C	Num	.	.	4.0	4.0	4.0	.	4.0	4.0	4.0	24.0
		Mean	.	.	41.3	43.5	45.3	.	45.2	50.0	46.1	45.2
		St Dev	.	.	3.7	3.1	0.9	.	4.1	2.5	3.1	3.8
	Room	Num	.	.	2.0	3.0	4.0	.	4.0	4.0	4.0	21.0
		Mean	.	.	32.4	29.3	42.8	.	40.6	44.6	31.0	37.6
		St Dev	.	.	7.2	1.2	2.3	.	1.1	3.3	5.3	7.0
Surface	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	46.5	.	.	.	.	.	.	.	.	46.5
		St Dev	4.8	.	.	.	.	.	.	.	.	4.8
	4 C	Num	.	4.0	.	4.0	4.0	4.0	3.0	4.0	4.0	27.0
		Mean	.	41.7	.	49.1	44.2	46.3	43.4	38.5	31.8	42.1
		St Dev	.	4.9	.	1.8	2.8	2.6	2.7	1.9	0.4	5.9
	Room	Num	.	4.0	.	4.0	4.0	4.0	5.0	4.0	4.0	29.0
		Mean	.	35.6	.	39.0	34.1	40.4	37.5	32.8	26.6	35.2
		St Dev	.	3.5	.	4.2	4.4	9.0	4.8	1.3	3.2	6.1

Stability of Tetrachloroethylene in Environmental Water Samples



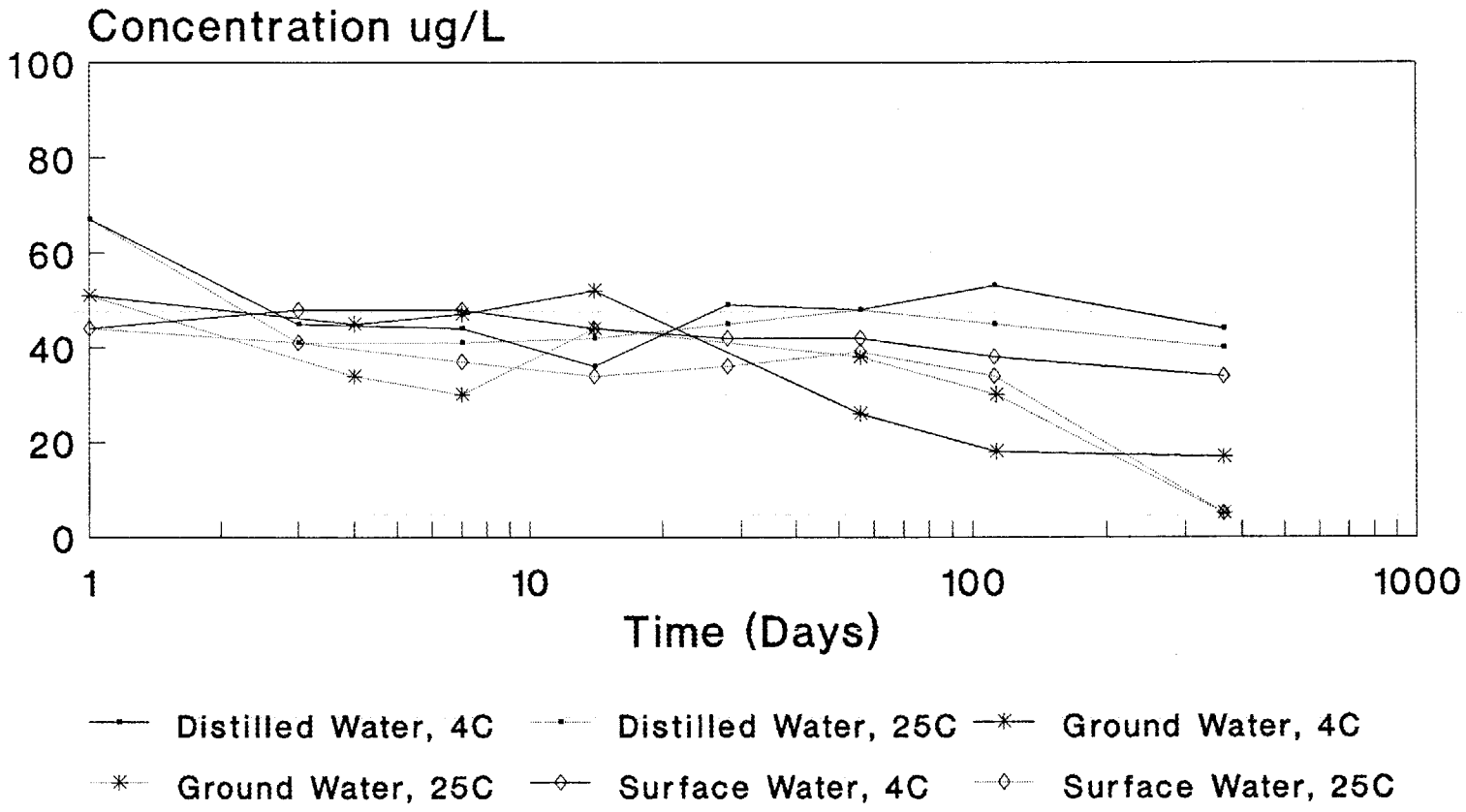
Initial Spike: 50 ug/L

Figure B.12

Table B.13 Summary Statistics for low level concentrations (μg/L) for Toluene.

			Days									
			0	3	4	7	14	28	56	112	365	All
Water	Storage											
Distilled	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	66.9	.	.	.	.	.	.	.	.	66.9
		St Dev	2.1	.	.	.	.	.	.	.	.	2.1
	4 C	Num	.	4.0	.	4.0	4.0	2.0	4.0	4.0	4.0	26.0
		Mean	.	44.9	.	44.1	35.9	48.9	48.2	53.3	44.1	45.4
		St Dev	.	1.1	.	2.3	2.8	2.0	0.4	2.4	0.6	5.5
	Room	Num	.	4.0	.	4.0	4.0	3.0	4.0	4.0	4.0	27.0
		Mean	.	41.1	.	41.2	42.1	45.0	47.8	44.7	39.7	43.0
		St Dev	.	1.8	.	5.0	5.6	1.4	0.3	3.7	2.9	4.1
Ground	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	51.4	.	.	.	.	.	.	.	.	51.4
		St Dev	3.1	.	.	.	.	.	.	.	.	3.1
	4 C	Num	.	.	4.0	4.0	4.0	.	4.0	4.0	4.0	24.0
		Mean	.	.	45.1	47.4	52.0	.	25.7	17.9	16.8	34.1
		St Dev	.	.	3.3	1.3	1.3	.	4.8	2.5	3.6	15.0
	Room	Num	.	.	2.0	3.0	4.0	.	3.0	4.0	4.0	20.0
		Mean	.	.	34.0	29.8	44.3	.	37.5	30.1	5.0	29.4
		St Dev	.	.	8.9	2.4	0.7	.	2.9	4.7	2.6	13.9
Surface	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	44.2	.	.	.	.	.	.	.	.	44.2
		St Dev	3.8	.	.	.	.	.	.	.	.	3.8
	4 C	Num	.	4.0	.	4.0	4.0	4.0	3.0	4.0	4.0	27.0
		Mean	.	47.9	.	48.2	44.5	42.5	41.7	38.3	34.0	42.5
		St Dev	.	4.3	.	1.1	2.3	2.6	1.8	1.9	0.6	5.3
	Room	Num	.	4.0	.	4.0	4.0	4.0	5.0	4.0	4.0	29.0
		Mean	.	41.2	.	37.3	34.5	35.8	38.9	33.7	4.7	32.5
		St Dev	.	3.6	.	4.7	2.5	4.0	2.7	2.9	2.6	12.0

Stability of Toluene in Environmental Water Samples



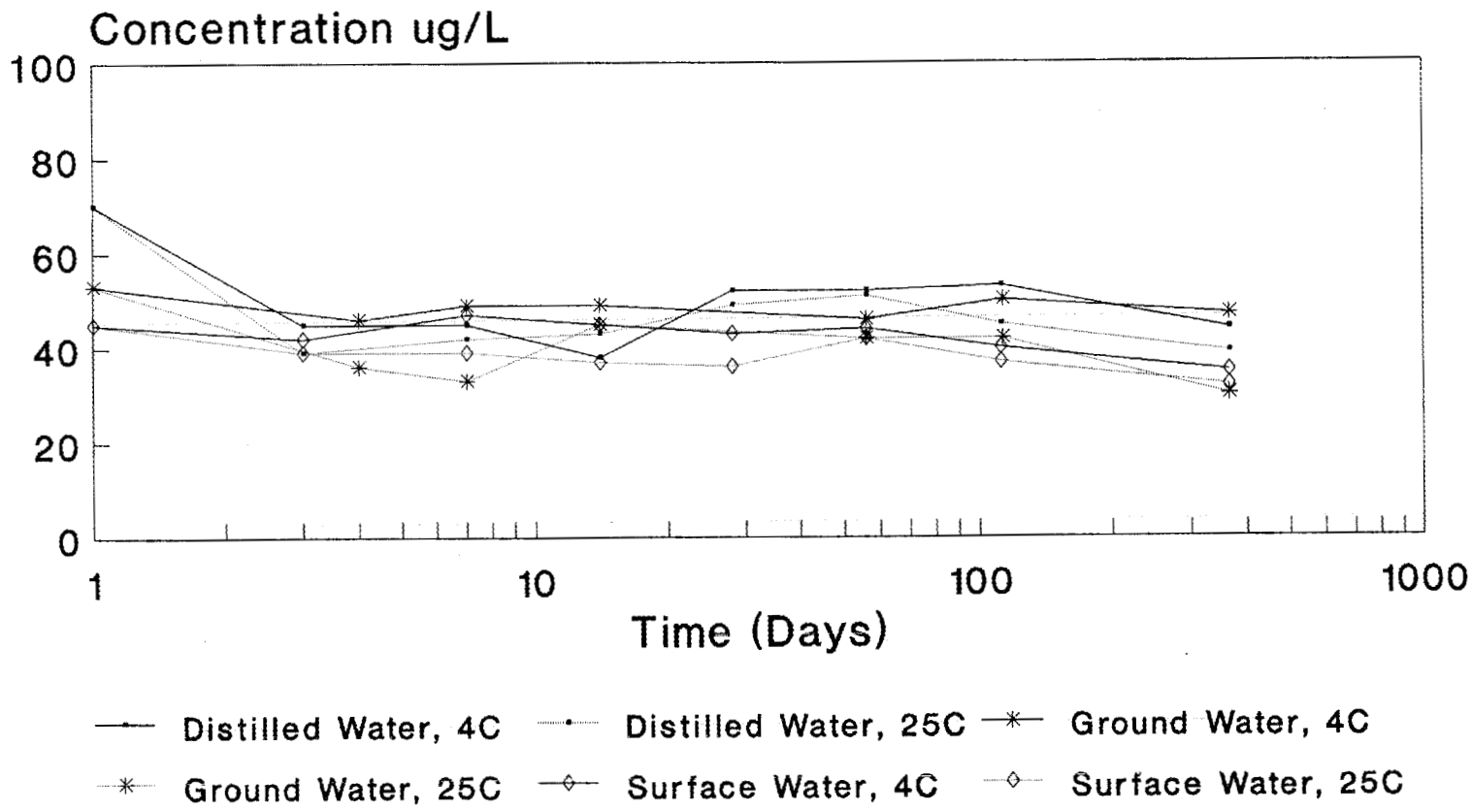
Initial Spike: 50 ug/L

Figure B.13

Table B.14 Summary Statistics for low level concentrations ($\mu g/L$) for Chlorobenzene.

			Days									
			0	3	4	7	14	28	56	112	365	All
Water	Storage											
Distilled	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	69.7	.	.	.	.	.	.	.	.	69.7
		St Dev	1.8	.	.	.	.	.	.	.	.	1.8
	4 C	Num	.	4.0	.	4.0	4.0	2.0	4.0	4.0	4.0	26.0
		Mean	.	44.5	.	44.6	38.0	52.0	51.8	52.7	44.0	46.4
		St Dev	.	1.4	.	2.6	2.9	2.0	0.5	2.7	0.4	5.5
	Room	Num	.	4.0	.	4.0	4.0	3.0	4.0	4.0	4.0	27.0
		Mean	.	39.3	.	41.5	43.4	49.1	51.4	45.2	39.0	43.9
		St Dev	.	2.1	.	5.5	6.1	2.2	0.4	3.5	3.3	5.6
Ground	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	52.7	.	.	.	.	.	.	.	.	52.7
		St Dev	2.7	.	.	.	.	.	.	.	.	2.7
	4 C	Num	.	.	4.0	4.0	4.0	.	4.0	4.0	4.0	24.0
		Mean	.	.	46.3	49.3	48.6	.	45.7	50.4	47.5	48.0
		St Dev	.	.	2.8	2.2	1.4	.	1.7	1.5	1.8	2.4
	Room	Num	.	.	2.0	3.0	4.0	.	3.0	4.0	2.0	18.0
		Mean	.	.	36.2	33.4	45.3	.	42.1	41.6	29.7	39.2
		St Dev	.	.	9.0	1.3	0.8	.	1.1	5.1	4.4	6.3
Surface	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	45.4	.	.	.	.	.	.	.	.	45.4
		St Dev	3.8	.	.	.	.	.	.	.	.	3.8
	4 C	Num	.	4.0	.	4.0	4.0	4.0	3.0	4.0	4.0	27.0
		Mean	.	42.3	.	47.4	44.8	42.8	43.8	40.5	35.2	42.4
		St Dev	.	3.4	.	1.7	2.5	3.7	1.7	1.7	0.8	4.3
	Room	Num	.	4.0	.	4.0	4.0	4.0	5.0	4.0	2.0	27.0
		Mean	.	38.8	.	38.5	37.1	35.7	41.7	37.4	31.9	37.9
		St Dev	.	2.3	.	3.7	1.6	4.1	2.7	1.5	1.1	3.5

Stability of Chlorobenzene in Environmental Water Samples



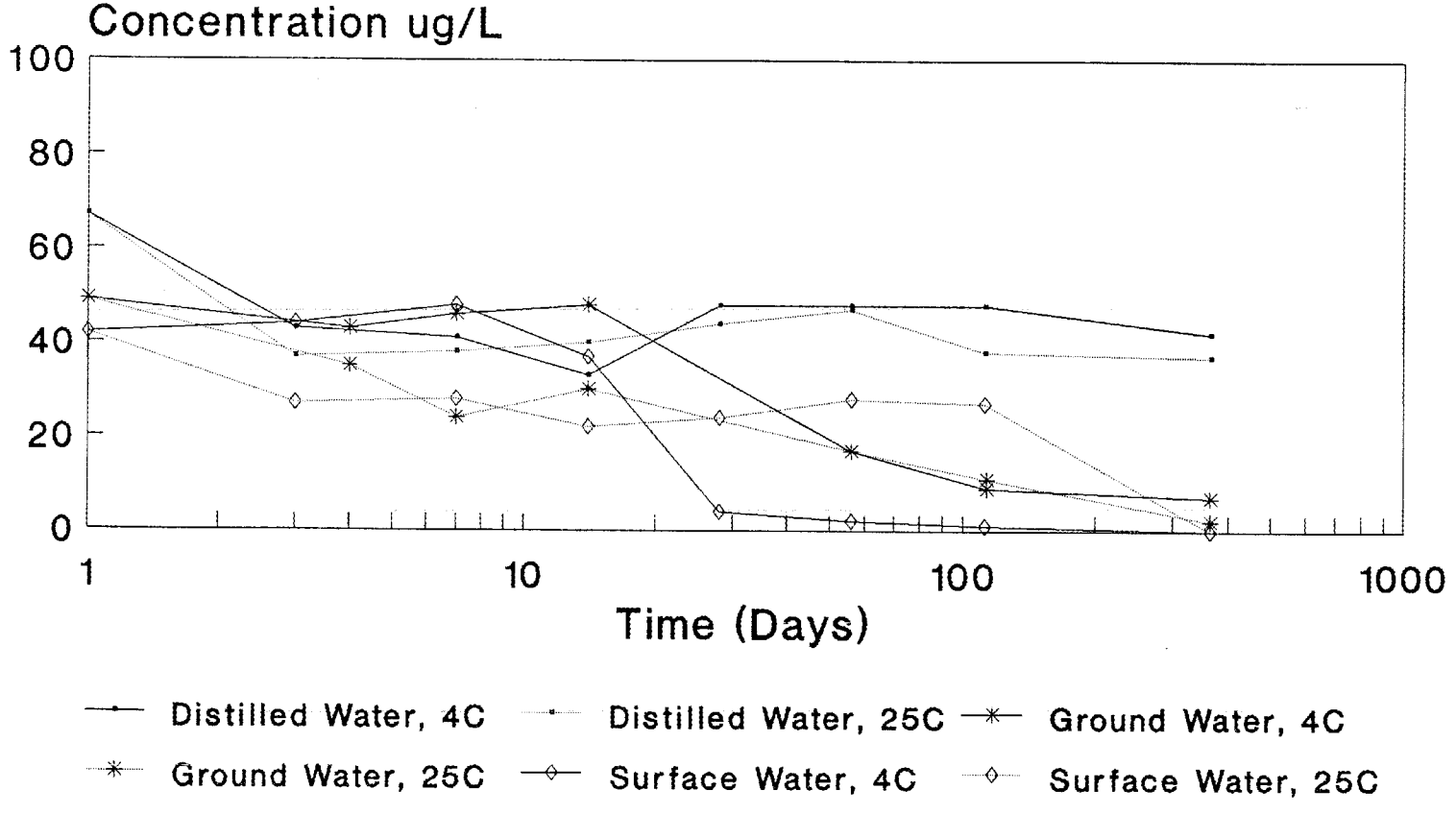
Initial Spike: 50 ug/L

Figure B.14

Table B.15 Summary Statistics for low level concentrations (μg/L) for Ethylbenzene.

Water	Storage		Days 0	3	4	7	14	28	56	112	365	All
Distilled	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	67.3	.	.	.	.	.	.	.	.	67.3
		St Dev	2.7	.	.	.	.	.	.	.	.	2.7
	4 C	Num	.	4.0	.	4.0	4.0	2.0	4.0	4.0	4.0	26.0
		Mean	.	42.8	.	41.3	33.5	48.0	47.7	47.6	41.9	42.9
		St Dev	.	1.9	.	2.5	2.8	2.1	0.5	2.5	0.7	5.2
	Room	Num	.	4.0	.	4.0	4.0	3.0	4.0	4.0	4.0	27.0
		Mean	.	36.6	.	38.4	40.0	43.8	46.7	38.2	37.0	40.0
		St Dev	.	2.4	.	5.6	6.7	1.5	0.2	2.7	2.9	4.9
Ground	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	48.7	.	.	.	.	.	.	.	.	48.7
		St Dev	3.6	.	.	.	.	.	.	.	.	3.6
	4 C	Num	.	.	4.0	4.0	4.0	.	4.0	4.0	4.0	24.0
		Mean	.	.	43.0	45.8	47.7	.	17.2	9.2	7.0	28.3
		St Dev	.	.	3.6	2.2	1.0	.	6.9	4.8	5.0	18.3
	Room	Num	.	.	2.0	3.0	4.0	.	2.0	4.0	4.0	19.0
		Mean	.	.	34.8	24.0	29.7	.	17.1	10.6	1.6	18.1
		St Dev	.	.	7.8	1.5	1.2	.	2.3	6.2	0.1	12.3
Surface	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	42.2	.	.	.	.	.	.	.	.	42.2
		St Dev	4.4	.	.	.	.	.	.	.	.	4.4
	4 C	Num	.	4.0	.	4.0	4.0	4.0	3.0	4.0	4.0	27.0
		Mean	.	44.4	.	47.9	36.8	4.5	2.2	1.5	0.0	20.3
		St Dev	.	4.9	.	3.9	3.8	0.8	2.1	0.1	0.0	21.2
	Room	Num	.	4.0	.	4.0	4.0	4.0	4.0	2.0	4.0	26.0
		Mean	.	26.9	.	28.5	22.1	23.6	27.9	27.3	0.1	22.0
		St Dev	.	3.3	.	3.3	2.4	2.8	1.8	1.5	0.1	10.0

Stability of Ethylbenzene in Environmental Water Samples



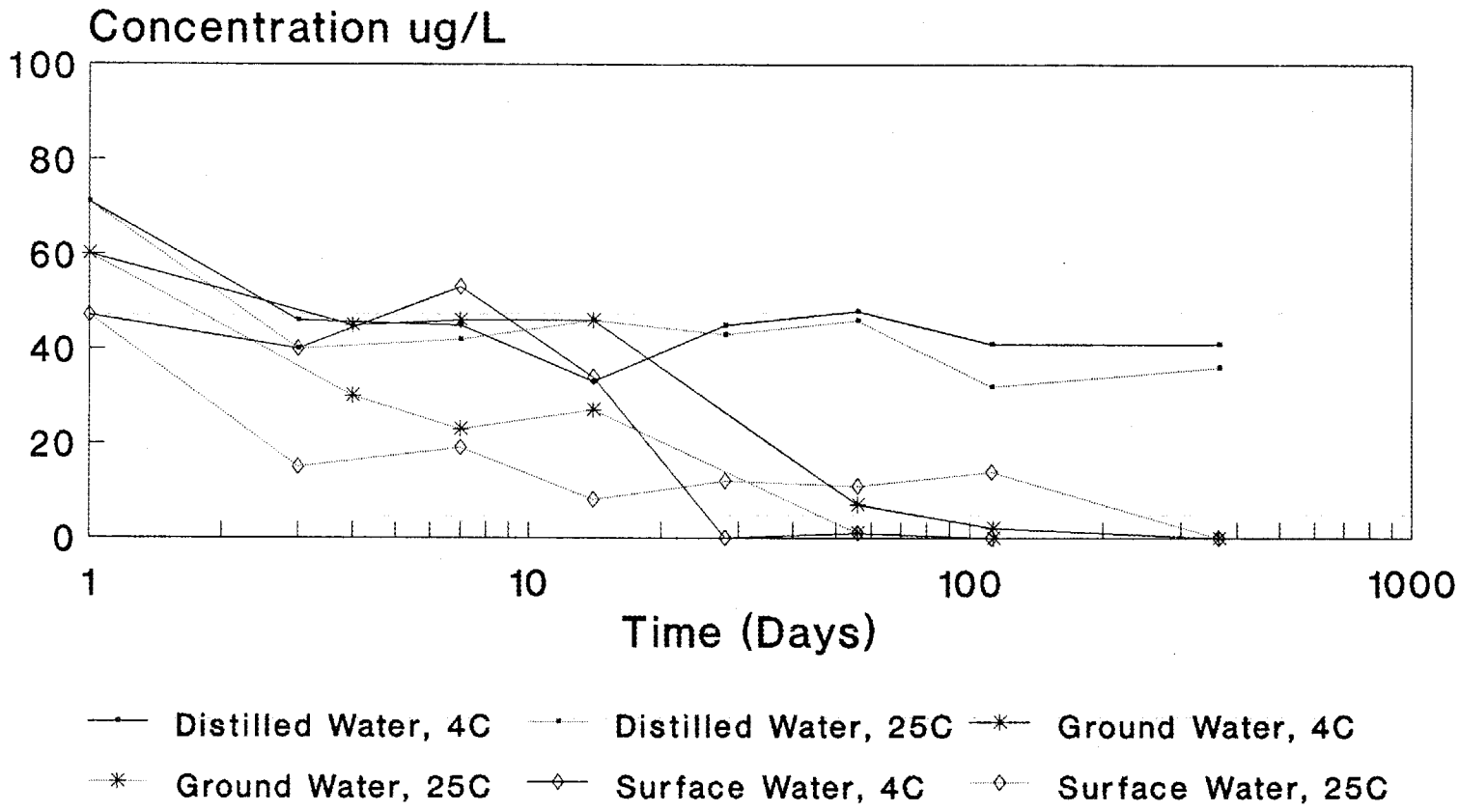
Initial Spike: 50 ug/L

Figure B.15

Table B.16 Summary Statistics for low level concentrations (μg/L) for Styrene.

Water	Storage		Days 0	3	4	7	14	28	56	112	365	All
Distilled	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	71.0	.	.	.	.	.	.	.	.	71.0
		St Dev	1.7	.	.	.	.	.	.	.	.	1.7
	4 C	Num	.	4.0	.	4.0	3.0	2.0	4.0	4.0	4.0	25.0
		Mean	.	45.9	.	44.8	32.6	45.4	47.8	41.0	41.1	42.9
		St Dev	.	1.4	.	2.6	4.7	2.3	0.3	7.0	0.9	5.5
	Room	Num	.	4.0	.	4.0	4.0	3.0	4.0	3.0	4.0	26.0
		Mean	.	40.4	.	41.6	45.6	43.0	46.5	32.1	35.8	40.9
		St Dev	.	2.2	.	5.9	6.6	1.2	0.2	6.3	2.4	6.1
Ground	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	60.1	.	.	.	.	.	.	.	.	60.1
		St Dev	1.6	.	.	.	.	.	.	.	.	1.6
	4 C	Num	.	.	4.0	4.0	4.0	.	4.0	4.0	4.0	24.0
		Mean	.	.	45.5	46.4	46.1	.	7.4	2.4	0.0	24.6
		St Dev	.	.	3.6	5.3	1.0	.	7.3	4.3	0.1	22.3
	Room	Num	.	.	2.0	3.0	4.0	.	3.0	4.0	4.0	20.0
		Mean	.	.	29.6	22.9	27.4	.	0.8	0.0	0.0	12.0
		St Dev	.	.	8.8	0.6	0.9	.	0.7	0.0	0.0	13.6
Surface	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	47.0	.	.	.	.	.	.	.	.	47.0
		St Dev	3.6	.	.	.	.	.	.	.	.	3.6
	4 C	Num	.	4.0	.	4.0	4.0	4.0	3.0	4.0	4.0	27.0
		Mean	.	40.3	.	52.7	33.9	0.4	0.9	0.2	0.0	19.0
		St Dev	.	3.6	.	4.5	5.9	0.3	1.0	0.1	0.0	22.1
	Room	Num	.	4.0	.	4.0	4.0	4.0	5.0	2.0	4.0	27.0
		Mean	.	15.4	.	19.2	8.4	12.0	11.0	13.9	0.0	11.2
		St Dev	.	5.2	.	9.4	6.4	3.5	6.4	2.4	0.1	7.7

Stability of Styrene in Environmental Water Samples



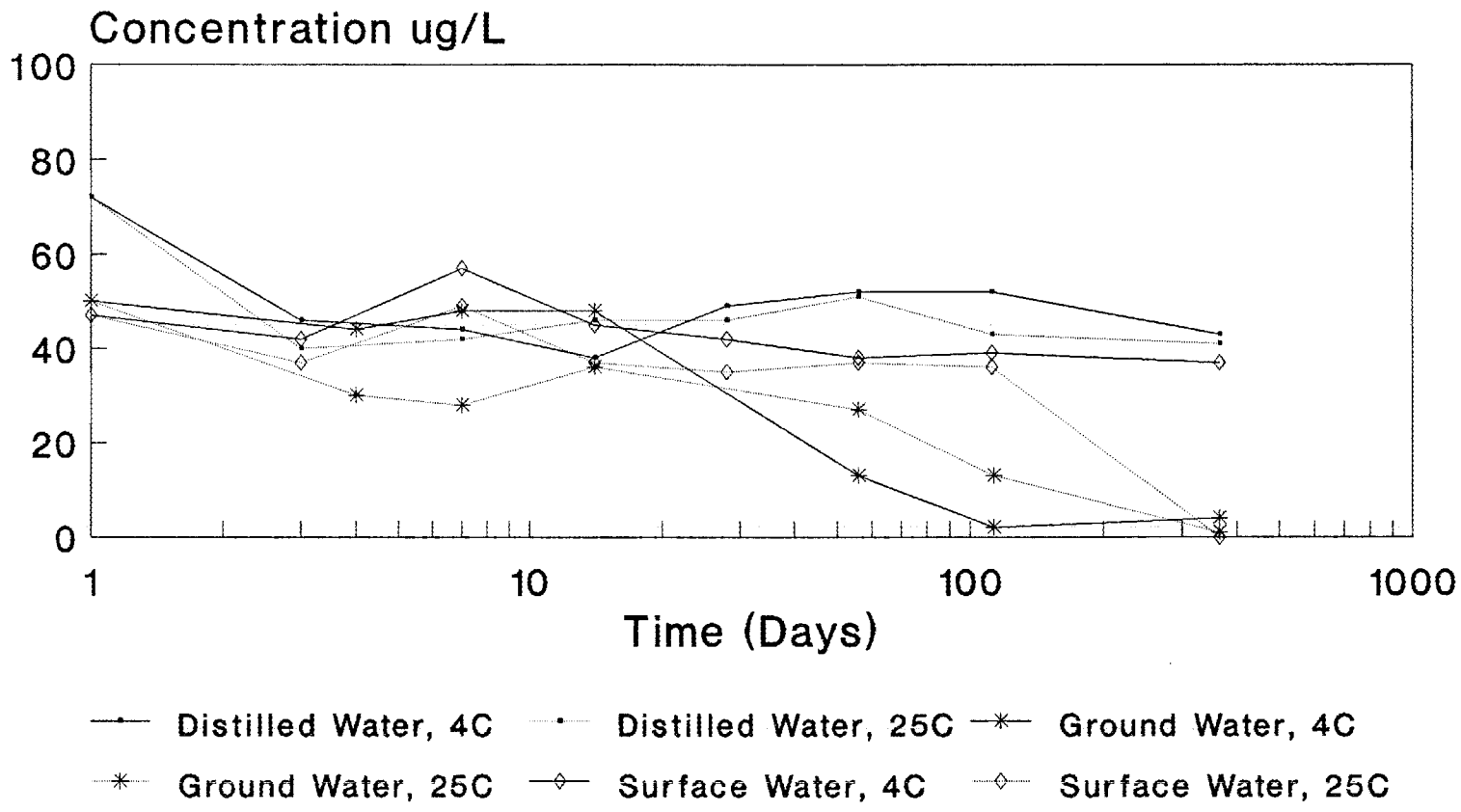
Initial Spike: 50 ug/L

Figure B.16

Table B.17 Summary Statistics for low level concentrations (μg/L) for <u>O-Xylene</u>.

Water	Storage		Days 0	3	4	7	14	28	56	112	365	All
Distilled	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	71.8	.	.	.	.	.	.	.	.	71.8
		St Dev	1.8	.	.	.	.	.	.	.	.	1.8
	4 C	Num	.	4.0	.	4.0	4.0	2.0	4.0	4.0	4.0	26.0
		Mean	.	46.1	.	44.3	37.5	48.7	51.9	51.8	43.3	46.0
		St Dev	.	1.9	.	2.6	3.5	2.2	0.8	5.0	0.6	5.5
	Room	Num	.	4.0	.	4.0	4.0	3.0	4.0	4.0	4.0	27.0
		Mean	.	40.5	.	41.6	46.2	45.9	51.1	42.9	40.8	44.1
		St Dev	.	2.5	.	6.0	6.9	2.6	0.3	4.1	2.3	5.2
Ground	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	50.3	.	.	.	.	.	.	.	.	50.3
		St Dev	3.2	.	.	.	.	.	.	.	.	3.2
	4 C	Num	.	.	4.0	4.0	4.0	.	4.0	4.0	4.0	24.0
		Mean	.	.	43.6	48.1	48.2	.	12.5	2.2	3.7	26.4
		St Dev	.	.	3.0	1.8	0.9	.	7.5	1.3	2.4	21.2
	Room	Num	.	.	2.0	3.0	4.0	.	3.0	4.0	4.0	20.0
		Mean	.	.	29.6	27.9	36.5	.	26.8	13.3	1.2	21.4
		St Dev	.	.	8.2	2.1	0.9	.	1.5	5.2	0.1	13.2
Surface	None	Num	4.0	.	.	.	.	.	.	.	.	4.0
		Mean	47.1	.	.	.	.	.	.	.	.	47.1
		St Dev	4.0	.	.	.	.	.	.	.	.	4.0
	4 C	Num	.	4.0	.	4.0	4.0	4.0	3.0	4.0	4.0	27.0
		Mean	.	42.2	.	57.2	45.2	42.4	37.5	38.9	37.0	43.1
		St Dev	.	3.3	.	4.8	4.5	3.8	5.4	1.1	0.9	7.3
	Room	Num	.	4.0	.	4.0	4.0	4.0	5.0	4.0	4.0	29.0
		Mean	.	37.4	.	49.4	36.6	35.0	36.9	36.0	0.1	33.2
		St Dev	.	4.4	.	6.1	2.3	3.8	2.2	4.6	0.2	14.6

Stability of o-Xylene in Environmental Water Samples



Initial Spike: 50 ug/L

Figure B.17

Appendix C

Data for Individual Organic Compounds

(Hydrochloric Acid Preservation)

TABLE C.1

HYDROCHLORIC ACID PRESERVATION OF AQUEOUS VOLATILES

WATER 1: DISTILLED WATER

COMPOUND	MEAN CONCENTRATIONS, UG/L			
	Day 0	Day 14	Day 28	Day 56
Bromomethane	65+/-1	47+/-3	49+/-1	37+/-0
Chloroethane	78+/-1	59+/-2	63+/-3	48+/-1
1,1-Dichloroethene	71+/-1	58+/-2	58+/-1	51+/-1
1,1-Dichloroethane	77+/-1	64+/-2	63+/-2	55+/-1
Chloroform	70+/-1	57+/-2	60+/-2	50+/-1
Carbon Tetrachloride	63+/-1	63+/-1	59+/-2	47+/-1
1,2-Dichloropropane	62+/-1	59+/-2	53+/-1	51+/-1
Trichloroethene	59+/-1	53+/-2	50+/-0	45+/-1
Benzene	60+/-2	53+/-2	53+/-1	49+/-1
1,1,2-Trichloroethane	62+/-3	60+/-3	59+/-2	49+/-1
Bromoform	54+/-2	56+/-2	59+/-2	44+/-0
1,1,2,2-Tetrachloroethane	61+/-4	61+/-4	59+/-1	51+/-2
Tetrachloroethene	57+/-1	49+/-1	46+/-1	40+/-0
Toluene	57+/-1	50+/-1	49+/-1	46+/-1
Chlorobenzene	54+/-0	50+/-1	49+/-1	41+/-1
Ethyl benzene	54+/-1	48+/-1	46+/-1	41+/-0
Styrene	44+/-1	39+/-2	36+/-2	32+/-1
Xylene	54+/-1	48+/-2	45+/-1	42+/-1

TABLE C.2

HYDROCHLORIC ACID PRESERVATION OF AQUEOUS VOLATILES

WATER 2: GROUND WATER

COMPOUND	MEAN CONCENTRATIONS, UG/L			
	Day 0	Day 14	Day 28	Day 56
Bromomethane	66+/-2	47+/-1	48+/-2	35+/-1
Chloroethane	78+/-2	58+/-3	66+/-2	45+/-2
1,1-Dichloroethene	71+/-3	50+/-5	58+/-2	48+/-4
1,1-Dichloroethane	74+/-1	64+/-2	64+/-1	56+/-2
Chloroform	69+/-2	58+/-2	60+/-1	52+/-3
Carbon Tetrachloride	62+/-1	62+/-3	59+/-3	44+/-2
1,2-Dichloropropane	62+/-1	58+/-1	54+/-1	60+/-1
Trichloroethene	62+/-1	54+/-1	53+/-1	43+/-2
Benzene	57+/-1	49+/-2	50+/-1	52+/-3
1,1,2-Trichloroethane	63+/-3	61+/-3	61+/-0	62+/-3
Bromoform	55+/-2	58+/-2	61+/-2	46+/-8
1,1,2,2-Tetrachloroethane	64+/-2	63+/-1	61+/-2	72+/-9
Tetrachloroethene	57+/-1	49+/-1	45+/-0	37+/-2
Toluene	55+/-1	48+/-1	49+/-1	48+/-2
Chlorobenzene	55+/-1	51+/-1	50+/-1	41+/-7
Ethyl benzene	51+/-1	45+/-1	46+/-0	40+/-2
Styrene	41+/-1	35+/-1	32+/-0	28+/-1
Xylene	51+/-1	46+/-1	45+/-0	41+/-2

TABLE C.3

HYDROCHLORIC ACID PRESERVATION OF AQUEOUS VOLATILES

WATER 3: SURFACE WATER

COMPOUND	MEAN CONCENTRATIONS, UG/L			
	Day 0	Day 14	Day 28	Day 56
Bromomethane	50+/-1	48+/-2	40+/-1	31+/-1
Chloroethane	63+/-1	61+/-2	52+/-2	40+/-0
1,1-Dichloroethene	60+/-1	54+/-1	50+/-3	45+/-0
1,1-Dichloroethane	65+/-1	59+/-1	57+/-1	51+/-1
Chloroform	60+/-1	53+/-1	53+/-2	51+/-1
Carbon Tetrachloride	58+/-1	52+/-1	54+/-3	47+/-0
1,2-Dichloropropane	58+/-1	53+/-2	64+/-5	49+/-0
Trichloroethene	58+/-1	49+/-2	57+/-3	46+/-1
Benzene	55+/-0	49+/-2	55+/-2	48+/-1
1,1,2-Trichloroethane	59+/-1	52+/-2	65+/-5	52+/-0
Bromoform	59+/-1	46+/-1	56+/-4	47+/-0
1,1,2,2-Tetrachloroethane	57+/-1	52+/-2	60+/-4	52+/-1
Toluene	51+/-1	47+/-1	53+/-1	47+/-1
Chlorobenzene	54+/-1	48+/-0	53+/-4	43+/-1
Ethyl benzene	51+/-0	47+/-1	51+/-1	45+/-0
Styrene	45+/-3	39+/-1	37+/-1	32+/-0
Xylene	54+/-2	48+/-2	51+/-0	44+/-0

(Surface water was not spiked with tetrachloroethene.)

Appendix D

Data for Individual Volatile Organic Compounds

(Sodium Bisulfate Preservation)

TABLE D.1

SUMMARY OF BISULFATE PRESERVATION OF AQUEOUS VOLATILES

WATER 1: DISTILLED WATER

COMPOUND	MEAN CONCENTRATIONS, UG/L					
	Day 1	Day 7	Day 14	Day 28	Day 56	Day 112
Chloromethane	192.02	87.85	88.05	90.50	194.37	99.10
Bromomethane	93.03	80.36	77.05	75.93	101.25	74.02
Chloroethane	112.56	98.55	84.95	88.10	121.63	103.20
Methylene Chloride	108.51	103.45	117.20	106.64	98.26	81.14
Acetone	173.12	178.33	158.60	125.59	179.69	145.18
Carbon Disulfide	299.67	253.69	217.95	176.67	236.42	144.49
1,1-Dichloroethene	108.51	107.19	98.92	85.65	110.79	86.47
1,1-Dichloroethane	117.33	123.87	119.39	95.92	114.36	109.33
Chloroform	130.72	139.74	133.42	111.87	124.37	126.05
2-Butanone	238.69	256.57	243.24	217.56	282.23	202.97
Carbon Tetrachloride	103.00	103.65	104.24	91.65	102.70	92.08
1,2-Dichloropropane	101.82	108.97	112.14	95.68	105.86	91.49
Trichloroethene	93.05	93.75	92.73	83.24	90.18	80.79
1,1,2-Trichloroethane	100.90	107.85	107.81	106.09	106.77	94.24
Benzene	95.97	97.90	95.54	99.11	106.46	94.34
Bromoform	104.43	104.88	105.81	108.62	111.43	101.28
4-Methyl-2-pentanone	274.21	324.95	320.74	328.13	345.88	296.45
2-Hexanone	313.10	362.46	357.43	265.62	374.15	320.99
Tetrachloroethene	86.69	89.38	79.40	66.63	74.19	71.88
1,1,2,2-Tetrachloroethane	101.13	113.04	107.91	116.62	112.34	110.48
Toluene	88.33	92.41	83.65	93.91	95.78	93.79
Chlorobenzene	85.82	91.42	83.58	86.71	87.13	86.64
Ethyl benzene	81.67	86.73	77.95	90.87	90.98	91.75
Styrene	82.70	85.75	80.94	93.25	96.65	94.06
Xylene	88.70	92.92	86.69	90.69	100.84	100.87

TABLE D.2

SUMMARY OF BISULFATE PRESERVATION OF AQUEOUS VOLATILES

WATER 2: SURFACE WATER

COMPOUND	MEAN CONCENTRATIONS, UG/L					
	Day 1	Day 7	Day 14	Day 28	Day 56	Day 112
Chloromethane	186.90	83.78	86.14	90.90	129.01	88.00
Bromomethane	92.82	78.67	75.48	74.57	70.18	77.65
Chloroethane	114.76	94.62	84.47	84.96	79.41	108.73
Methylene Chloride	113.29	102.49	121.46	106.55	97.04	85.29
Acetone	194.67	168.88	168.05	131.36	176.35	162.99
Carbon Disulfide	318.35	234.09	212.48	172.52	178.51	150.67
1,1-Dichloroethene	123.49	106.84	101.77	82.90	53.93	85.84
1,1-Dichloroethane	124.63	119.37	120.31	94.58	83.53	109.72
Chloroform	112.18	111.51	110.17	89.26	76.22	107.68
2-Butanone	283.40	264.01	256.79	221.02	247.60	246.51
Carbon Tetrachloride	121.06	108.42	111.21	93.75	74.91	107.60
1,2-Dichloropropane	113.47	111.13	116.67	97.02	79.81	95.51
Trichloroethene	111.48	104.28	100.72	84.65	69.56	84.64
1,1,2-Trichloroethane	110.15	110.13	114.31	105.58	88.99	102.90
Benzene	105.09	98.85	99.80	88.71	66.74	88.61
Bromoform	118.77	115.50	113.20	106.21	96.10	105.48
4-Methyl-2-pentanone	324.94	340.49	335.39	346.68	303.44	325.52
2-Hexanone	376.12	376.76	375.64	276.12	318.82	352.10
Tetrachloroethene	93.57	91.13	79.33	67.07	60.05	74.27
1,1,2,2-Tetrachloroethane	110.88	113.05	109.35	111.95	102.54	110.81
Toluene	101.02	99.04	88.60	83.38	41.54	83.98
Chlorobenzene	97.09	100.52	90.09	83.65	65.69	86.90
Ethyl benzene	94.46	94.27	83.01	79.56	42.87	85.08
Styrene	94.03	94.10	92.06	76.39	22.95	88.05
Xylene	99.93	101.32	91.79	80.38	29.25	95.45

TABLE D.3

SUMMARY OF BISULFATE PRESERVATION OF AQUEOUS VOLATILES

WATER 3: GROUND WATER

COMPOUND	MEAN CONCENTRATIONS, UG/L					
	Day 1	Day 7	Day 14	Day 28	Day 56	Day 112
Chloromethane	176.09	79.39	82.00	88.05	145.44	116.54
Bromomethane	89.11	75.06	71.33	72.82	101.18	90.05
Chloroethane	110.52	93.53	81.54	81.38	120.32	124.37
Methylene Chloride	115.93	100.97	120.04	110.65	102.20	98.24
Acetone	198.33	156.91	160.38	123.40	185.49	168.56
Carbon Disulfide	305.80	222.83	203.17	170.60	223.58	151.68
1,1-Dichloroethene	115.60	101.05	96.66	80.79	106.61	94.69
1,1-Dichloroethane	122.45	113.79	113.85	91.73	115.29	108.50
Chloroform	110.59	107.37	107.41	87.84	101.48	117.66
2-Butanone	285.48	242.47	256.87	222.80	290.30	232.81
Carbon Tetrachloride	112.91	101.86	108.43	91.54	106.20	111.17
1,2-Dichloropropane	111.18	108.83	112.79	95.61	107.69	97.75
Trichloroethene	103.95	97.42	97.87	81.35	92.15	81.51
1,1,2-Trichloroethane	109.26	106.75	112.32	105.37	106.94	96.96
Benzene	103.12	98.22	98.24	89.58	96.39	86.32
Bromoform	115.95	110.56	110.35	104.37	116.49	105.43
4-Methyl-2-pentanone	327.78	317.61	333.86	330.78	360.92	313.64
2-Hexanone	372.96	342.19	368.07	262.64	402.57	339.66
Tetrachloroethene	89.28	86.95	78.26	67.54	74.34	70.88
1,1,2,2-Tetrachloroethane	111.74	110.41	111.52	112.97	116.31	114.18
Toluene	97.24	96.02	88.16	82.46	88.11	86.79
Chlorobenzene	93.90	96.94	88.43	82.27	89.17	85.28
Ethyl benzene	89.58	89.90	82.14	79.73	84.38	84.65
Styrene	89.68	88.62	83.77	76.11	87.39	85.59
Xylene	96.55	97.25	91.00	81.13	92.92	91.66

Appendix E

Data for Individual Volatile Organic Compounds

(Ascorbic Acid Preservation)

TABLE E.1

SUMMARY OF ASCORBIC ACID PRESERVATION OF AQUEOUS VOLATILES

WATER 1: DISTILLED WATER

COMPOUND	MEAN CONCENTRATIONS, UG/L					
	Day 1	Day 7	Day 14	Day 28	Day 56	Day 112
Chloromethane	58.69	148.32	91.57	31.60	126.86	87.37
Bromomethane	223.61	89.95	79.29	97.05	86.43	71.58
Chloroethane	84.47	114.00	99.28	96.29	103.57	91.57
Methylene Chloride	91.08	94.85	108.04	90.04	99.13	103.25
Acetone	121.34	182.10	108.54	114.11	249.63	466.07
Carbon Disulfide	176.51	318.80	261.49	189.49	213.67	144.44
1,1-Dichloroethene	80.14	113.07	108.78	82.06	94.22	78.14
1,1-Dichloroethane	110.93	118.76	124.25	99.04	109.63	109.87
Chloroform	121.95	127.89	139.63	114.17	122.81	125.78
2-Butanone	214.55	284.66	231.03	137.00	246.34	201.30
Carbon Tetrachloride	47.68	66.68	71.56	47.58	35.29	29.87
1,2-Dichloropropane	98.20	110.07	119.33	94.63	103.08	98.77
Trichloroethene	96.67	106.20	106.74	77.54	89.43	76.09
1,1,2-Trichloroethane	99.08	107.44	117.56	97.92	96.16	93.02
Benzene	91.73	98.21	102.66	83.01	86.93	78.59
Bromoform	1.59	25.04	58.80	20.25	9.88	16.12
4-Methyl-2-pentanone	282.86	339.79	336.07	259.40	277.27	249.87
2-Hexanone	287.88	371.81	385.36	230.82	344.67	235.45
Tetrachloroethene	97.82	97.40	101.56	74.09	81.85	75.76
1,1,2,2-Tetrachloroethane	105.28	117.12	119.67	100.35	95.77	95.64
Toluene	92.33	96.86	97.85	79.51	81.80	77.99
Chlorobenzene	90.84	94.04	100.55	79.25	80.02	76.11
Ethyl benzene	87.61	92.84	95.67	75.19	75.27	73.78
Styrene	79.61	76.32	85.73	58.26	51.26	43.92
Xylene	94.06	99.52	102.23	78.92	83.09	86.44

TABLE E.2

SUMMARY OF ASCORBIC ACID PRESERVATION OF AQUEOUS VOLATILES

WATER 2: SURFACE WATER

COMPOUND	MEAN CONCENTRATIONS, UG/L					
	Day 1	Day 7	Day 14	Day 28	Day 56	Day 112
Chloromethane	103.52	122.21	87.81	129.75	123.82	88.98
Bromomethane	72.05	87.29	75.73	95.04	86.73	73.02
Chloroethane	94.59	115.54	95.75	95.52	103.60	83.21
Methylene Chloride	92.93	96.35	109.37	92.16	96.21	108.37
Acetone	143.66	192.52	125.35	112.68	169.40	163.86
Carbon Disulfide	252.11	288.93	235.50	189.46	207.67	148.06
1,1-Dichloroethene	99.14	109.73	110.24	89.64	100.15	85.22
1,1-Dichloroethane	109.82	118.19	125.52	101.97	109.35	112.84
Chloroform	98.22	105.22	114.89	96.00	100.46	103.96
2-Butanone	242.16	289.74	271.07	150.41	246.10	194.54
Carbon Tetrachloride	45.20	83.69	95.05	84.90	81.78	81.04
1,2-Dichloropropane	98.89	114.10	124.33	98.03	104.85	100.78
Trichloroethene	96.53	108.77	109.89	82.92	92.62	77.98
1,1,2-Trichloroethane	99.98	110.67	126.73	105.06	98.92	95.71
Benzene	90.39	101.50	105.43	91.89	92.23	84.23
Bromoform	1.69	11.70	28.47	55.66	10.44	20.26
4-Methyl-2-pentanone	318.10	356.13	385.97	295.58	286.14	252.98
2-Hexanone	322.48	399.19	445.81	266.33	355.91	245.72
Tetrachloroethene	90.75	91.94	94.66	70.94	76.94	70.91
1,1,2,2-Tetrachloroethane	111.84	121.01	131.89	108.50	97.06	95.34
Toluene	92.42	99.06	98.45	85.86	87.64	80.53
Chlorobenzene	91.05	97.87	102.00	86.43	87.93	81.67
Ethyl benzene	89.33	95.33	96.55	82.26	82.43	77.93
Styrene	81.06	94.11	101.54	87.23	78.23	78.69
Xylene	93.35	100.36	103.82	84.36	88.60	88.32

TABLE E.3

SUMMARY OF ASCORBIC ACID PRESERVATION OF AQUEOUS VOLATILES

WATER 3: GROUND WATER

COMPOUND	MEAN CONCENTRATIONS, UG/L					
	Day 1	Day 7	Day 14	Day 28	Day 56	Day 112
Chloromethane	90.34	118.25	56.31	128.55	124.07	82.48
Bromomethane	67.89	84.76	73.59	92.99	89.11	71.31
Chloroethane	83.52	113.45	89.42	93.41	106.41	82.98
Methylene Chloride	98.70	95.08	110.34	95.70	100.54	111.45
Acetone	146.81	199.08	117.22	115.07	182.58	171.47
Carbon Disulfide	245.93	283.34	223.89	190.00	204.03	133.49
1,1-Dichloroethene	97.82	110.77	106.18	87.56	99.13	78.58
1,1-Dichloroethane	106.45	115.30	119.92	102.77	110.26	110.20
Chloroform	96.52	103.86	113.26	95.52	99.58	103.18
2-Butanone	266.39	302.29	267.93	153.27	253.94	206.71
Carbon Tetrachloride	45.05	87.14	93.54	84.57	82.73	81.57
1,2-Dichloropropane	102.35	113.67	123.30	97.10	109.42	100.43
Trichloroethene	99.77	106.56	107.73	78.21	94.36	76.80
1,1,2-Trichloroethane	106.50	111.34	123.08	104.03	100.09	97.65
Benzene	92.89	102.15	103.73	90.01	96.13	85.59
Bromoform	1.54	21.66	30.32	29.87	7.51	10.77
4-Methyl-2-pentanone	341.86	366.83	374.74	303.72	285.08	259.33
2-Hexanone	352.12	411.94	425.42	277.03	354.49	250.01
Tetrachloroethene	90.43	92.63	91.29	71.06	76.16	69.26
1,1,2,2-Tetrachloroethane	120.26	124.53	128.16	109.91	99.58	97.81
Toluene	96.55	99.62	97.71	85.43	88.56	80.73
Chlorobenzene	91.81	98.48	100.22	86.74	85.21	80.25
Ethyl benzene	92.65	97.48	95.13	81.71	82.05	77.64
Styrene	78.99	94.15	99.16	85.28	76.14	77.79
Xylene	96.99	103.08	102.36	83.36	87.55	87.35

Appendix F

Estimation of Maximum Pre-analytical Holding Times Using a Cubic Spline Fit

Estimation of Maximum Pre-analytical Holding Times Using a Cubic Spline Fit

The problems encountered with fitting zero-order and first-order models to the preanalytical holding time data are illustrated in Figure F-1 for low-level concentrations of ethylbenzene in ground water stored at 4°C. The concentrations are approximately constant for the first 14 days then rapidly decrease to a plateau of about 10 ug/L. Basically, there are only two concentration levels. Both the zero-order and first-order models try to average these low and high concentrations levels.

To approximate the rapidly decreasing concentrations, additional linear models were examined which had derivatives that also decreased rapidly. The zero-order model, first-order model, and the additional models are given in Table F-1. The log-term model and inverse-term model were able to approximate the rapid concentration decreases for some of the special cases. However, these models couldn't approximate any cases which had an initial constant-concentration plateau. An empirical model was then applied which had an initial constant-concentration for days less than day = D_0, and a final concentration for days greater than day = D_1. The concentrations between day = D_0 and day = D_1 were modelled by a cubic spline which is a cubic polynomial with a sigmoidal shape curve. The cubic spline starts at the initial concentration at day = D_0 and ends at the final concentration at day = D_1. In addition, the cubic spline is required to be continuous at day = D_0 and day = D_1.

Table F-1. Models and their derivatives used to approximate special cases of VOC's in water.

Model	Equation	Derivative
Zero-Order	$C = C_0 + B(day)$	$dC/d(day) = B$
First-Order	$C = C_0 exp[B(day)]$	$dC/d(day) = BC_0 exp[B(day)]$
Log-Term	$C = C_0 + B(day) + Aln(day)$	$dC/d(day) = B + A/(day)$
Inverse-Term	$C = C_0 + B(day) + A/(day)$	$dC/d(day) = B - A/(day)2$

Mathematically, the cubic spline approximates the concentrations by a function of time, f(D) with D = day:

$$f(D) = \begin{cases} C_0 & \text{If } D \leq D_0 \\ a + bD + cD^2 + eD^3 & \text{If } D_0 < D < D_1 \\ C_1 & \text{If } D \geq D_1. \end{cases}$$

The continuity condition and initial and final concentration conditions places two restrictions on f(D):

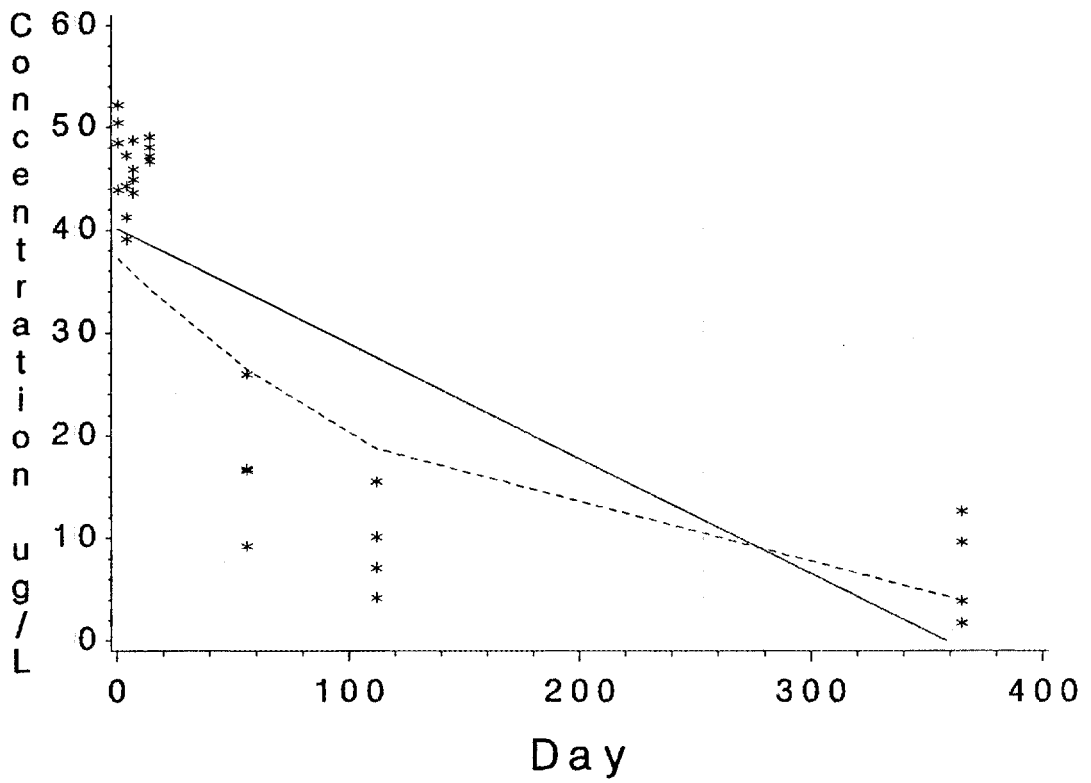


Figure F-1. Low concentrations of ethylbenzene in groundwater at 4° C. A zero-order model (solid line) and first order model (dashed line) are fitted to the concentration data (stars).

1. $f(D_0) = C_0$ and $f(D_1) = C_1$.

2. $f'(D_0) = 0$ and $f'(D_1) = 0$, where f' is the derivative with respect to D_0 and D_1, respectively.

Using these two restrictions for the cubic spline, the coefficients a, b, c, and e can be determined in terms of D_0 and D_1.

$$a = (C_0H_1 - C_1H_0)/(H_1 - H_0) \qquad c = -1.5(C_1 - C_0)(D_0 + D_1)/(H_1 - H_0)$$

$$b = 3(C_1 - C_0)D_0D_1/(H_1 - H_0) \qquad e = (C_1 - C_0)/(H_1 - H_0)$$

where $H_0 = 0.5D_0^2(3D_1 - D_0)$ and $H_0 = 0.5D_1^2(3D_0 - D_1)$.

The estimates of the parameters D_0 and D_1 for the cubic splines are calculated by the method of non-linear least squares. The cubic splines were estimated for the 14 special cases of VOC in water samples using the non-linear procedure PROC NLIN with METHOD=MARQUARDT in the SAS computer programming language [*12*]. The

results of fitting a cubic spline to low-level concentrations of ethylbenzene in ground water at 4°C are plotted in Figure F-2.

Maximum Holding Time

The ASTM and ESE definitions for MHT are adapted to the cubic spline using the following procedures:

ASTM MHT procedure for the cubic spline:

1. Fit the data with a cubic spline using C_0 = the average of concentrations on day = 0 and C_1 = the average of concentrations on day = 365 or one-half the average for concentrations of day = 112 and day = 365.

2. Construct a 99% confidence interval about the initial concentration $C_0 \pm t(0.005,df)S_p/\ n$ where t(0.005,df) is the 99.5 percentile point of the t-distribution with df degrees of freedom for S_p. The pooled standard deviation, S_p, is estimated from all within standard deviations for days $\leq D_0$ and n is the number of observations on day = 0.

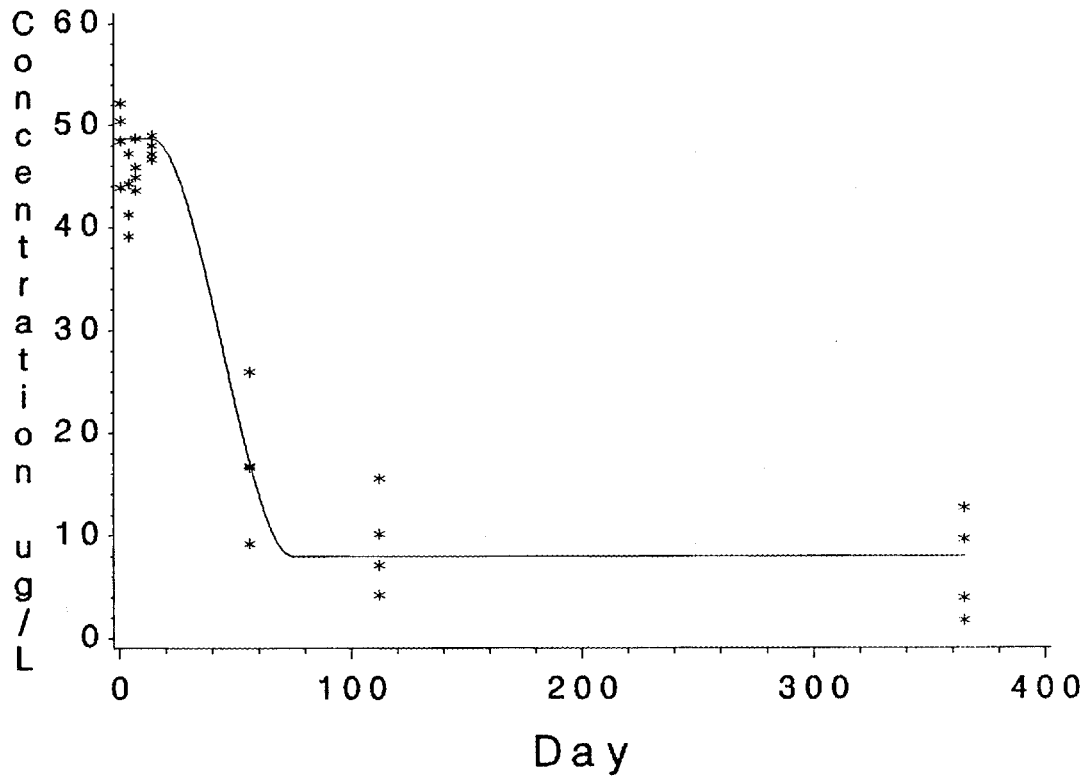


Figure F-2. Cubic spline fitted to low-level concentrations of ethylbenzene in ground water stored at 4° C.

3. The MHT is found by iteratively calculating the cubic spline for days in the interval (D_0,D_1) until the following conditions are achieved:

   a) $C_0 - t(0.005,df)S_p/\ n \leq f(MHT)$.

   b) $C_0 - t(0.005,df)S_p/\ n > f(MHT+1)$.

<u>ESE MHT procedure for the cubic spline</u>:

1. Fit the data with a cubic spline using C_0 = the average of concentrations on day = 0 and C_1 = the average of concentrations on day = 365, or one-half the averages for concentrations on day = 112 and day = 365.

2. Construct a ± 10% interval on C_0 [e.g., $(0.9C_0,1.1C_0)$]. Test that the 10% change is outside the 90% confidence interval on C_0 [e.g., $0.1C_0 \geq t(0.05,df)S_p/\ n$ where t(0.05,df) is the 95 percentile point of the t-distribution

with df degrees of freedom for S_p. The pooled standard deviation, S_p, is estimated from all within standard deviations for days $\leq D_0$ and n is the number of observations on day = 0.

3. If a 10% change is not outside the 90% confidence interval on C_0, calculate the concentration change (i.e. $C_0 - KC_0$) that is outside the 90% confidence interval by:

$$K = t(0.05,df)S_p/(C_0\ n)$$

If $K > 0.15$, the cubic spline model does not give an appropriate fit for estimating MHT.

4. The MHT is defined as the one-sided lower 90% confidence interval on the critical time (i.e., the day the cubic spline equals $C_0 - KC_0$). This MHT definition is equivalent to the day the lower 90% confidence interval on the cubic spline equals $C_0 - KC_0$. The MHT is found by iteratively calculating the cubic spline for days in the interval (D_0,D_1) until the following conditions are achieved:

a) $C_0 - KC_0 \leq f(MHT) - t(0.10,df)\{Var[f(MHT)]\}^{1/2}$.

b) $C_0 - KC_0 > f(MHT+1) - t(0.10,df)\{Var(f(MHT+1)]\}^{1/2}$.

The value of t(0.10,df) is the 90 percentile point of the t-distribution with df = N - 2 degrees of freedom for N observations in the data set. The variance of the cubic spline Var[f(D)] is calculated by error propagation formulas [*13*] using the derivatives with respect to D_0 and D_1.

$$Var[f(D)] = (df/dD_0)^2Var(D_0) + (df/dD_1)^2Var(D_1) + 2(df/dD_0)(df/dD_1)Cov(D_0,D_1).$$

The variance terms $Var(D_0)$,$Var(D_1)$ and covariance term $Cov(D_0,D_1)$ are estimated from the non-linear least squares fit of the cubic spline to the observed data. The derivatives of the cubic spline are:

$$(df/dD_0) = da/dD_0 + (db/dD_0)D + (dc/dD_0)D^2 + (de/dD_0)D^3, \text{ and}$$

$$(df/dD_1) = da/dD_1 + (db/dD_1)D + (dc/dD_1)D^2 + (de/dD_1)D^3.$$

Let $K = 1/(D_0 - D_1)^4$, then the derivatives of the coefficients are:

$$da/dD_0 = 6K(C_1 - C_0)D_0D_1^2 \qquad dc/dD_0 = 6K(C_1 - C_0)(D_0 + 2D_1)$$

$$db/dD_0 = -6K(C_1 - C_0)D_1(2D_0 + D_1) \qquad de/dD_0 = -6K(C_1 - C_0)$$

$$da/dD_1 = -6K(C_1 - C_0)D_0^2D_1 \qquad dc/dD_1 = -6K(C_1 - C_0)(2D_0 + D_1)$$

$$db/dD_1 = 6K(C_1 - C_0)D_0(D_0 + 2D_1) \qquad de/dD_1 = 6K(C_1 - C_0)$$

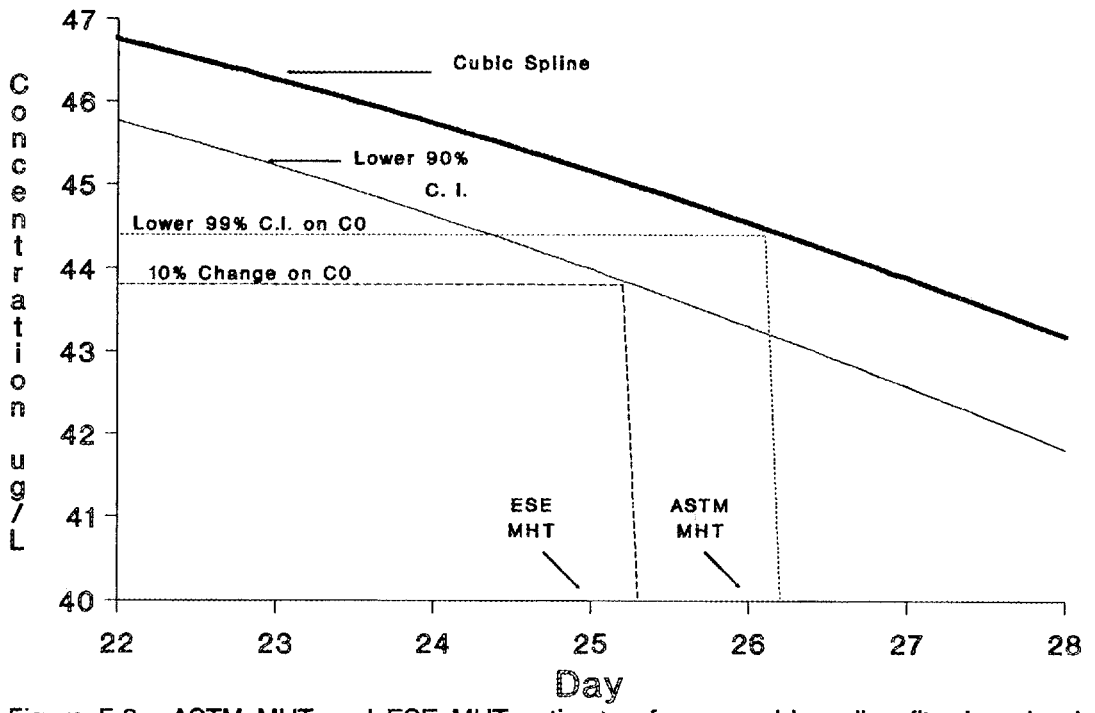


Figure F-3. ASTM MHT and ESE MHT estimates from a cubic spline fit. Low level concentrations of ethylbenzene in ground water stored at 4° C.

Figure F-3 illustrates the ASTM and ESE definitions for low-level concentrations of ethylbenzene in ground water stored at 4°C. The maximum holding times for the special cases of volatile organic compounds are tabulated in Table F-2.

Table F-2. Cubic spline estimates of MHT days for special cases of volatile organic compounds in water.

Volatile Organic Compound	Level	Water	Storage	D_0	D_1	ASTM MHT	ESE MHT
1,1,2-Trichloroethane	High	Distilled	Room	0.00	48.17	14	8
1,1,2,2-Tetrachloroethane	High	Distilled	4°C	0.00	19.14	7	3
1,1,2,2-Tetrachloroethane	High	Distilled	Room	0.50	3.00	1	1
Ethylbenzene	High	Surface	4°C	11.76	45.73	22	11
Carbon Tetrachloride	Low	Surface	Room	0.00	74.56	30	15
1,1,2,2-Tetrachloroethane	Low	Distilled	4°C	0.00	45.78	15	7
1,1,2,2-Tetrachloroethane	Low	Distilled	Room	0.00	3.00	1	0
Ethylbenzene	Low	Ground	4°C	14.00	74.61	26	25
Ethylbenzene	Low	Surface	4°C	8.68	32.21	14	12
Styrene	Low	Ground	4°C	0.00	37.98	6	5
Styrene	Low	Surface	4°C	6.19	30.03	11	9
Styrene	Low	Surface	Room	1.23	3.80	2	1
Acetone	Ascorbic	Distilled	4°C	28.00	95.65	41	30
Carbon Tetrachloride	Ascorbic	Distilled	4°C	(a)	(a)	<14	<7

(a) Cubic spline was inappropriate for this data, but bounds on MHT can be estimated.

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